Combustion Characteristics of some Imported Feedstocks and Short Rotation Coppice (SRC) Willow for UK Power Stations

By

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The candidate confirms that the work submitted is his/her own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others. Further details of the jointly-authored publications and the contributions of the candidate and the other authors to the work are listed below.

Chapter 4 is based on two publications:

GUDKA, B., DARVELL, L. I., JONES, J. M., WILLIAMS, A., KILGALLON, P. J., SIMMS, N. J. & LARYEA-GOLDSMITH, R. 2012. Fuel characteristics of wheat-based Dried Distillers Grains and Solubles (DDGS) for thermal conversion in power plants. Fuel Processing Technology, 94, 123-130.

I was lead author and lead conductor and co-ordinator of most experiments and all experimental data respectively.

Fluidised Bed combustion studies were done at Cranfield. (*This will not be included in the thesis*)

DARVELL, L. I., JONES, J. M., GUDKA, B., BAXTER, X. C., SADDAWI, A., WILLIAMS, A. & MALMGREN, A. 2010. Combustion properties of some power station biomass fuels. Fuel, 89, 2881-2890.

I carried out a lot of the experimental work (proximates, ultimates, TGA pyrolysis studies, kinetic calculations using the constant reaction rate method, Py GC-MS and char preparation and was the lead co-ordinator for all the experimental data.

Leilani Darvell was the lead author and conducted the char nitrogen work.

Xiaomian Baxter assisted with the char preparation and conducted the metal analysis for the fuels.

Abha Saddawi assisted with the kinetic calculations using the Senum and Yang approximation.

Chapter 5 is based on a conference paper but with the complete data set of results included.

GUDKA, B., JONES, J. M., MOHAMMED, A., NORFOLK, J., BARRACLOUGH, T., RICHE, A., SHIELLD, I. & YATES, N. 2010b. Combustion Characteristics and Combustion Related Problems for Short Rotation Coppice (SRC) Willow. Proccedings of the 18th European Biomass Conference Lyon, France

I was lead author and also lead conductor and co-ordinator of experiments and experimental data respectively

The metal analyses data was provided by Rothamsted Research

Chapter 6 is based on a conference paper but with more data included.

GUDKA, B., JONES, J. M., SHIELD, I., TRYBUSH, S. O., YATES, N. E., ALLISON, G., CLIFTON-BROWN, J., DONNISON, I. & MORRIS, C. 2010c. The effect of biochemical composition and ash composition on the thermal conversion options for different genotypes of willow. Proceedings of the Bioten Conference, Birmingham, UK.

I was lead author and also lead conductor and co-ordinator of experiments and experimental data respectively.

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ABSTRACT

The availability and sustainability of biomass is very crucial in the production of energy using biomass. Currently nearly two thirds of the biomass in the UK is being imported due to the limited supply of indigenous resources. The Green House Gas (GHG) emissions from importing these fuels are very high. The imported feed stocks studied here (PKE, shea, olive and DDGS) exhibited high N and ash contents and also high slagging and fouling tendencies which are undesirable fuel traits. The high N contents and S content (in the case of DDGS) emit NO_x and SO_x emissions respectively which cause acid rain and photochemical smog and are harmful to human health. Due to the poor quality of these fuels for use in boilers and furnaces, and the need for Green House Gas savings, indigenous fuels with better combustion properties need to be produced.

Energy crops like SRC willow and Miscanthus have remarkably better fuel properties (eg low ash and nitrogen contents) and there is potential to grow them in the UK. In order to help farmers to increase the yields and grow these crops in a more sustainable way, some agronomic studies have been carried out. The influence of 6 different fertilizer treatments with varying nitrogen levels, (0, 150 and 250 Kg/hectare), the addiition of K (150Kg N + 100Kg K), the addition of S (150 Kg N + 80 Kg S) and sewage pellets on SRC willow are studied. These crops are sampled twice a year for 3 years. It was found that fertilizer treatments do have an impact on the fuel properties (eg the application of N and K increase the C content and the CV of the fuel). Different parts of the crop also exhibit different fuel properties (eg leaves have higher nitrogen and ash contents which are undesirable qualities during combustion) hence it is important to avoid such parts. Sampling time also has a very big impact as the composition of the crop changes over the growth period. The optimum harvest time for SRC willow would be spring, after senescence when the leaves have fallen and some of the nutrients have translocated into the soil for the next growing season.

Different genotypes of SRC willow with varying biochemical compositions were also studied to enable farmers to try and breed different genotypes with desired fuel properties for the next generation. 6 genotypes with varying biochemical

composition (highest and lowest hemicelluloses, cellulose and lignin contents) were studied. From these, one genotype *S.elaeagnos Scop* showed remarkably different properties compared to the other 5 genotypes. All the genotypes except *S.elaeagnos Scop* had very high ash melting temperatures (>1500^{o}C) and low slagging and fouling tendencies. *S.elaeagnos Scop* exhibits good grinding properties. The pyrolysis products of SRC willow are highly sensitive to its hemicelluloses and lignin contents. Due to its different properties *S.elaeagnos Scop* is of great interest for further investigation especially for its grinding ability.

Overall, there is a potential for the UK to grow its own SRC willow. A larger dataset is required for the fertilizer application experiment to make firm conclusions since it is insufficiently small at the moment. A larger selection of genotypes would also need to be studied in order to help farmers breed a larger variety of SRC willow.

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Normanclature

DECC	Department of Energy and Climate Change
DEFRA	Department of Environmental, Food and Rural Affairs
GWP	Greenhouse Warming Potential
GHG	Green House Gas
SRC	Short Rotation Coppice
PKE	Palm Kernel Expellers
DDGS	Dried Distilllers Grains and Solubles
ADL	Acid Detergent Lignin
NDF	Neutral Detergent Fibre
ADF	Acid Detergent Fibre
ICP	Inductively Coupled Plasma Spectrometry
TGA	Thermogravimetric Analysis
DTA	Differential Thermogravimetric Analysis
STA-MS	Simultaneous Thermogravimetry Analyser coupled with a Mass Spectrometer
AFT	Ash Fusion Test
SST	Shrinkage start Temperature
DT	Deformation Temperature
HT	Hemisphere Temperature
FT	Flow Temperature
Py GC-MS	Pyrolysis Gas Chromatography-Mass Spectrometry

Treatment A 0 Kg N as $NH_4(NO_3)$

Treatment D 150 Kg N as $NH_4(NO_3)$

Treatment F 250 Kg N as $NH_4(NO_3)$

Treatment J 100 Kg K as K_2O + 150 Kg N $NH_4(NO_3)$

Treatment N 80 Kg SO_3 as $(NH_4)_2SO_4$ balanced to give 150 Kg N as $NH_4(NO_3)$

Treatment O Sewage pellets

Chapter 1

Introduction

1.1 Energy demand, security and policy

Energy is defined as the ability to do work. Humans require energy for daily activities like cooking, manufacturing goods, heating, cooling, utilising electrical equipment and transportation. This energy is mainly in the forms of electricity, petroleum or gas and is produced from fossil fuels (coal, oil and natural gas) or renewable (hydro, geothermal, wind biomass, solar and tidal) or as nuclear power.

The energy industry has evolved vastly since the pre-Industrial Revolution up until today. Before the Industrial Revolution, traditional biomass was the primary source of energy. Post Industrial Revolution (19^{th} century), coal was the first fossil fuel discovered to run the steam engine. Oil was the next energy source to be discovered in the early 20^{th} century along with the first automobile. It was the embargo introduced by some Arab countries to supply oil to Western countries that led to the discovery of gas, nuclear power and bioethanol. Currently the renewable energy sector is growing very fast and the investment made in this sector is four times that made in 1995 (Asif and Muneer, 2007, Solomon and Krishna, 2011).

This evolution in the energy sector has mainly come about due to:

- Advancement in technology leading to the requirement of high efficiency fuels
- Increase in global population leading to increasing energy demands
- Environmental concerns due to the large amount of greenhouse gases and other pollutants being emitted into the atmosphere
- Energy security, since the non-renewable resources will eventually be used up and other resources will be needed to meet the increasing energy demands.

1.1.1 World Energy Demand and Supply

According to the New Policies Scenario that outlines any recent commitments that have been made but not necessarily implemented within the years 2009-2035, the global population is predicted to increase from 6.8 billion in 2009 to 8.6 billion in 2035, a 26% growth. 90% of this growth will be from non-OECD (Organisation for Economic, Co-operation and Development) developing countries like India and

China. This growth in population will lead to a growth in energy demand of approximately 40% within the outlook period although the rate at which energy demand is growing will decelerate. From 2009-2020, the rate of growth of energy demand will be 1.8% per year but it will decrease to 0.9% per year from 2020-2035 (IEA, 2011). Figure 1.1 shows the energy demand by source from 1980 and during the New Policies scenario.

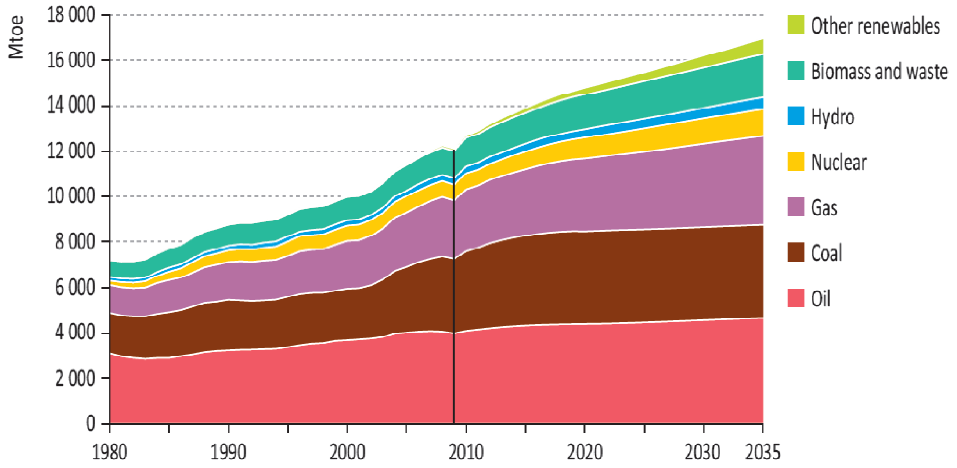


Figure 1 1 World primary energy demand by source for the New Policies Scenario (IEA, 2011)

It is predicted that the demand for each energy source will increase over the outlook period, although it may be at a decreasing rate for some of the sources as reported in Table 1.1. The % contribution of coal in the energy mix increases until it peaks at 28% early on in the outlook period, after which it falls to 24%. The % contribution of oil decreases over the outlook period while that of natural gas, nuclear and renewable sources increases. The % contribution of renewable sources doubles over the outlook period indicating that they have great potential for the energy industry.

Table 1 1 Increase in demand and the contribution of energy sources within the New Policies Scenario period (2009-2035) (IEA, 2011)

Source	Increase in Demand from 2009-2035	Contribution to the Global Energy mix		
		2009	2020	2035
Coal	25%	~25%	28%	24%
Oil	15 mb/day	33%		27%
Natural Gas	54%	21%		23%
Nuclear	73%	6%		7%
Renewables	1505 Mtoe	7%		14%

mb/day million barrels per day

Mtoe million tonnes oil equivalent

In the New Policies Scenario, hydro, wind and biomass are the major renewable energy sources, with China being the largest producer of renewable energy as shown in Figure 1.2 (IEA, 2011).

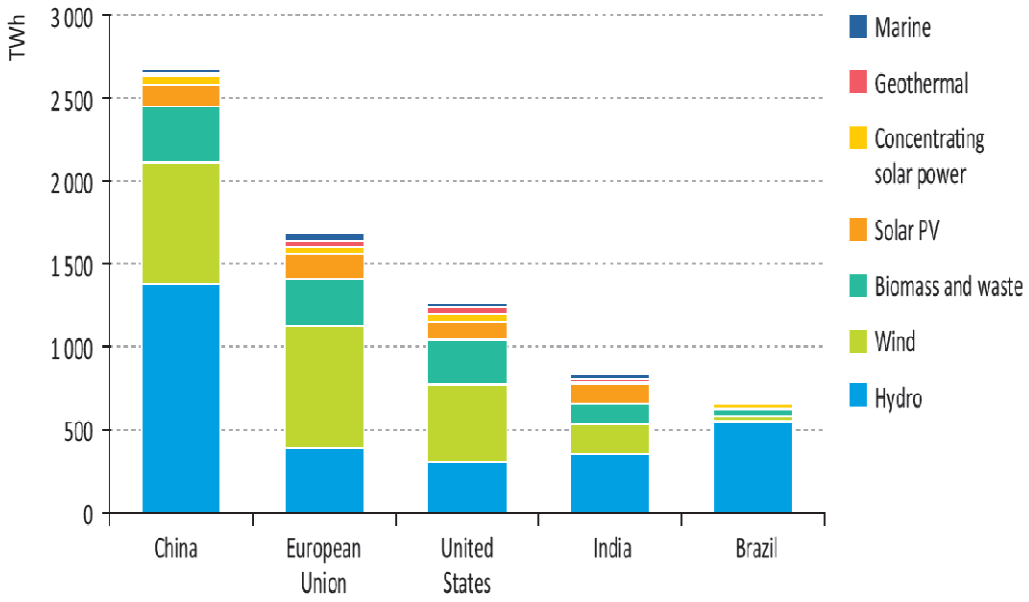


Figure 1 2 Largest Renewable Energy producers in New Policies Scenario (IEA, 2011)

1.1.2 UK Energy Consumption

The UK's energy consumption grew from 1980-2010 by 14Mtoe, but the sources of energy used changed over this period as shown in Figure 1.3 (DECC, 2011b). It is seen that the UK is moving to more efficient, sustainable and less carbon intensive energy sources.

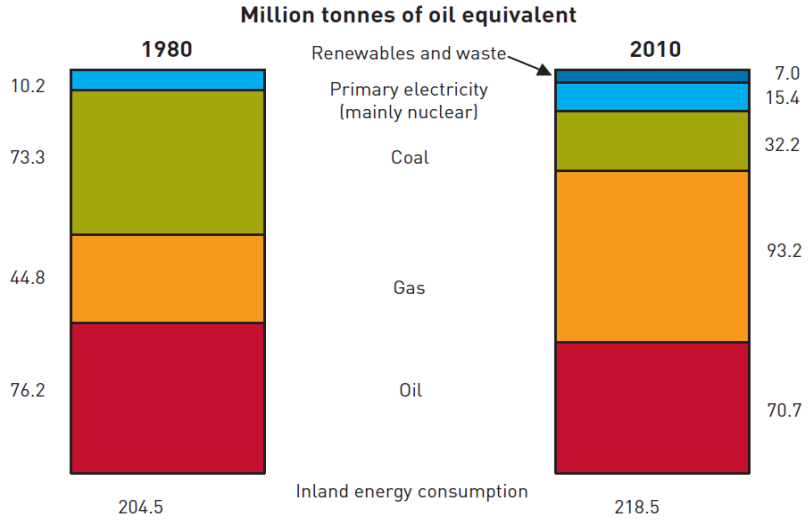


Figure 1 3 UK inland energy consumption for 1980 and 2010

According to Figure 1.3, the consumption of coal and oil fell by 41.1Mtoe and 5.5Mtoe respectively while that of natural gas, nuclear, and renewables and waste increased by 48.4Mtoe, 5.2Mtoe and 7Mtoe respectively. In 2010, the 3 main renewable energy sources were biomass, large scale hydro and wind as shown in Figure 1.4.

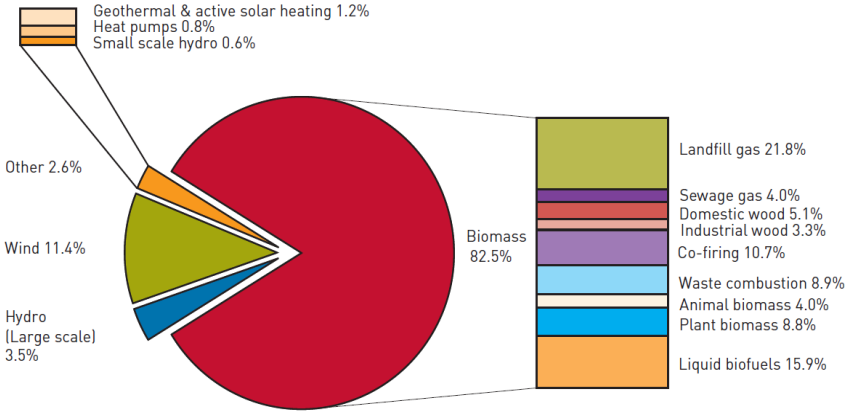


Figure 1 4 UK Renewable energy sources in 2010

According to the UK renewable energy roadmap, the UK aims to produce 15% of its energy consumed from renewable by 2020 and it has the potential to do so. 90% of this renewable energy can be produced from renewable transport, on-shore and off-shore winds, biomass heat and electricity, ground-source and air-source heat pumps, marine, and other renewables (including, hydro, geothermal, solar and domestic heat) (Huhne et al., 2011).

1.1.3 Energy Security

With this increasing demand in energy, the world cannot solely depend on fossil fuels which have been the primary energy sources till today. The availability of these fossil fuels is decreasing and we will eventually run out of them. It has been predicted that coal, oil and gas will be available for a further 107, 35 and 37 years respectively from 2005 onwards. Coal will last the longest and has reserves all around the world while oil which will last for the shortest period of time is mainly available in the Middle East. Due to this limited availability of fossil fuels, their prices will fluctuate regularly depending on their production and demand (Shafiee and Topal, 2009). To avoid these fluctuations, cheaper and more sustainable sources energy need to be found and renewable sources are attractive options in this regard.

1.2 Environmental Issues and Policy

Fossil fuels have deemed to be very problematic in terms of the environment. Some of these problems include:

1.2.1 Global Warming

Fossil fuels are very carbon intensive and their production and consumption emit greenhouse gases including carbon dioxide (CO_2), methane (CH_4) nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride (SF_6) which have led to global warming through the green house effect. The earth's global temperature has increased by 0.8^oC in the century after the first global warming was predicted and it is expected to increase by $1.1\text{-}6.4^oC$ in the century to come. This will have a detrimental effect on the population and some of

the eco-systems. Several countries have a target to limit the warming to 2°C relative to pre-industrial temperatures and this can only be achieved if the global greenhouse gas emissions peak before 2020, are cut by 50% by 2050 and are zero by 2100 (Wexler et al., 2010). The UK greenhouse gas emissions have shown a downward trend from 1990-2009 as shown in Figure 1.5 due to the substantial decline in energy consumption in all sectors and the change of electricity production from gas to coal to the use of nuclear (DECC, 2011a). These emissions are reported with the Global Warming Potential of each of the gases taken into account. The global warming potential (GWP) of a greenhouse gas is the ability of a unit mass of that particular gas to trap heat in the atmosphere as a ratio to the ability of one unit mass of CO_2 to trap heat in the atmosphere over a particular time interval (de_Richter and Caillol, 2011). The GWPs of these gases over a 100 year period and their atmospheric lifetime are listed in Table 1.2 (de_Richter and Caillol, 2011)

Table 1 2 GWP of some GHGs and their atmospheric lifetimes

Greenhouse Gas	GWP_{100}	Atmospheric lifetime (years)
CO_2	1	>100
CH_4	26	12
N_2O	298	114
CFC-12 or CCl_2F_2	10900	100
CFC-11 CCl_3F	4800	55
HCFC-22 or $CHClF_2$	1700	12
CFC-113 or CCl_2FCClF_2	4800	85
HFC-134a or CFH_2CF_3	1430	14
PFC-14 or CF_4	5700	50000
HCFC-142b or CH_3CF_2Cl	1800	18
SF_6	22800	3200

GWP Global Warming Potential

In 2009, 84% of UK greenhouse gas emissions were CO_2. 39% of these emissions were from the energy sector, 24% from transport, 16% from the residential use of fossil fuels and 16% from the business sector.

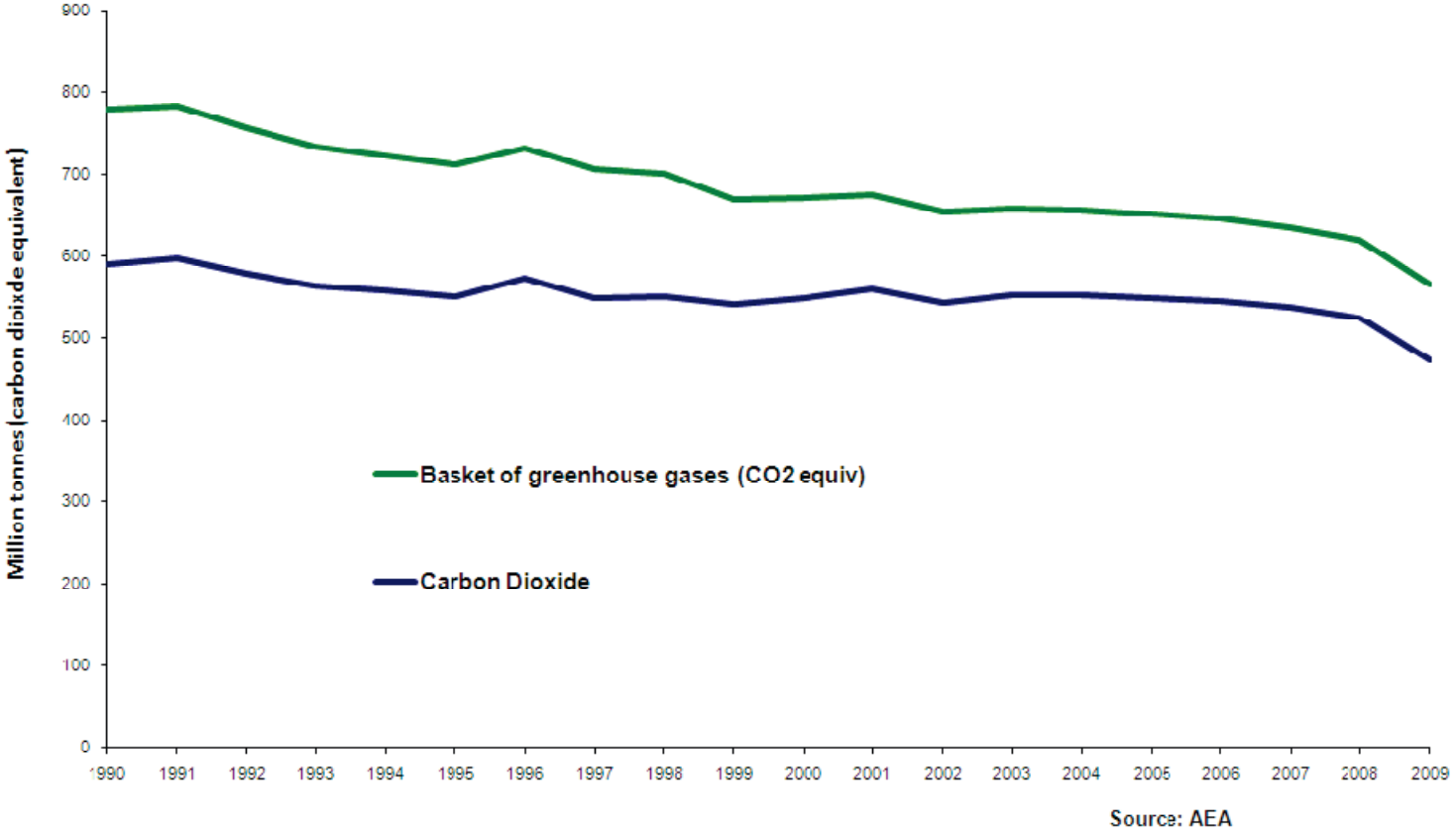


Figure 1 5 UK Greenhouse Gas Emissions and net CO_2 emissions from 1990-2009 (DECC, 2011a)

Since the energy sector is a large contributor to the CO_2 emissions, cleaner sources of energy are needed to be able to meet the 2^oC target for minimising global temperature rises.

1.2.2 Acid Rain and Photochemical Smog

Fossil fuels like coal have high sulphur and nitrogen contents of approximately 0.45-4.99% and 0.65-2.04% respectively (Varey et al., 1996). When burnt in air under high temperature conditions, the nitrogen in the fuel reacts with oxygen to form oxides of nitrogen. Approximately 95% of these oxides are nitrous oxide (N_2O) which is a greenhouse gas and the remaining 5% are nitric oxide (NO) and nitrogen dioxide (N_2O) (World Health and ebrary, 2006). These oxides react with moisture in the atmosphere to form acid rain which corrodes buildings and other surroundings. NO_2 can also cause inflammation of the lungs. Similarly sulphur oxides are formed when the S in the fuel reacts with oxygen. Sulphur dioxide (SO_2) reacts with the atmospheric oxygen to form sulphur trioxide (SO_3) which further reacts with water to form sulphuric acid which is also very corrosive and also forms acid rain. SO_3 can cause a person to cough and choke at concentrations as low as 1ppm (part per million).

1.2.3 Land and water contamination

The production, consumption and transportation of fossil fuels tend to contaminate land and water bodies. Some of these are discussed in Sections 1.2.3.1 and 1.2.3.2 .

1.2.3.1 Mining of coal

During underground mining of coal, subsidence of land occurs and causes destruction to the structures above such as roads and buildings. It also impacts the drainage of ground water and aquifers. Drainage water absorbs toxic compounds from the sub-surface strata and contaminates the ground water that it flows into. When mining is done above ground, noise pollution, soil erosion, ground water

contamination and destruction of aquifers occurs. Above ground mining also has a negative impact on the fertility of agricultural land (Bian et al., 2010).

1.2.3.2 Oil Contamination

Crude oil is the most utilised fuel in the world, but its presence in the environment can be very harmful to humans and ecosystems. From 1990-1999, 47% of oil pollution was caused by the slow release of the oil from its natural strata into the ecosystems (Peter, 2007). This does not have detrimental effects since the slow release allows the ecosystem to adapt. The most harmful sources of oil pollution are due to human activities including transporting the oil and other industrial activities. From 1990-1999, 12% of oil pollution was from its transportation (Peter, 2007). Oil can be transported via pipelines and tankers, the former being the more efficient and safer option. The latter is more prone to accidents in the seas which cause large spills; oil is also discharged from the operation of the tankers. The oil that is discharged forms a thin layer on the water surface inhibiting the entry of oxygen in the water hence killing marine animals. Entry of sunlight is also prevented by the oil resulting in killing the aquatic plants since they cannot photosynthesize. Some of the toxic compounds when ingested by marine animals can kill them. Birds' feathers can get coated with the oil making them heavy and preventing the birds from flying thereby making them easy prey. Food chains are also affected by the oil pollution as infected organisms are consumed by other consumers higher up in the food chain (Paul F, 2002, Peter, 2007, SUCHANEK, 1993)

Due to the increase in energy demand and all the problems encountered by fossil fuels, cleaner and more sustainable forms of energy need to be found, i.e the renewable sources like wind, hydro, biomass, solar and geothermal. Some of these sources, like wind and solar, are intermittent as they depend on the wind speed and amount of sunlight respectively. Biomass on its own, and also when it is co-fired, has high potential for producing heat and electricity, and biofuels can be used in the transportation sector.

1.3 Biomass

Biomass can generally be defined as any biological material that is living or has recently died and can be used directly as a fuel to produce heat and electricity or can be converted into biofuels for transport (Jenkins et al., 1998).

1.3.1 Why Biomass?

Compared to fossil fuels, biomass is considered to be a better fuel in several important ways. Firstly, it is carbon neutral, hence all the CO_2 emitted during its combustion is utilised for growing the biomass with no excess emissions released into the atmosphere, apart from fossil fuel inputs during its life-cycle. The NO_x and SO_x emissions from biomass are also low hence the problem of acid rain is reduced. It has a high volatile content (80%) which increases its ignition stability and makes its thermo-chemical conversion to methanol and hydrogen easier. It can also be converted to liquid biofuels via bio-chemical technologies (Zhang et al., 2010).. Co-firing of biomass with coal is an attractive process and can easily be retrofitted into existing power plants (Perry and Rosillo-Calle, 2008). There are some concerns of biomass supply but these can potentially be overcome as it is fast growing and readily available for use. Biomass in the form of waste helps to reduce landfill disposal hence freeing up land for other purposes. It also has the ability to re-establish contaminated land that is no longer productive and increase its soil fertility, water retention and biodiversity (Saidur et al., 2011).

1.3.2 Biomass Structure

Biomass has a lignocellulosic structure and is mainly composed of cellulose, hemicelluloses and lignin, with small amounts of lipids, proteins, starches, simple sugars, water, hydrocarbons (HCs), ash and other compounds (Jenkins et al., 1998).

Cellulose is a linear homopolymer of the monomer glucose. The fundamental building block in the structure of cellulose is cellubiose, a disaccharide of glucose. A natural cellulose structure consists of approximately 10,000 glucose units. The cellulose structures have a tendency to form intra and intermolecular hydrogen bonds which result in a molecular group to form microfibrilis. Microfibrilis can be

of two types, crystalline and amorphous depending on whether they have high or low packing densities respectively (Brown, 2003)

Hemicellulose is a hetropolysacchride composed of hexoses, pentoses and deoxyhexoses with a degree of polymerisation of 100-200. The hexoses include D-glucose, D-mannose and D-galactose while the pentoses are D-xylose, L-arabinose and D-arabinose and finally the deoxyhexoses include 6-deoxy-L-mannose and 6-deoxy-L-galactose. Some uronic acids are also found. Compared to hardwoods, softwoods have more mannose and galactose and, less xylose and acetylated hydroxyl groups. The main components of softwoods are glucomannan and xylan. When hydrolysed, hemicellulose releases more pentoses, while cellulose releases more hexoses. Due to its low polymerisation, it is less stable both thermally and chemically compared to cellulose (Brown, 2003).

Lignin is a phenylpropane polymer consisting of the monomers coniferyl alcohol, sinapyl alcohol and coumaryl alcohol. The most likely functional groups seen in lignin are phenolic, alcoholic hydroxyl and methoxy groups and aldehydes. Softwoods contain more phenolic hydroxyls, aliphatic hydroxyls and aldehydes and less methoxyls compared to hardwood. Lignin cannot be depolymerised and it protects the cellulose and hemicelluloses in the plant from being attacked by insects (Brown, 2003).

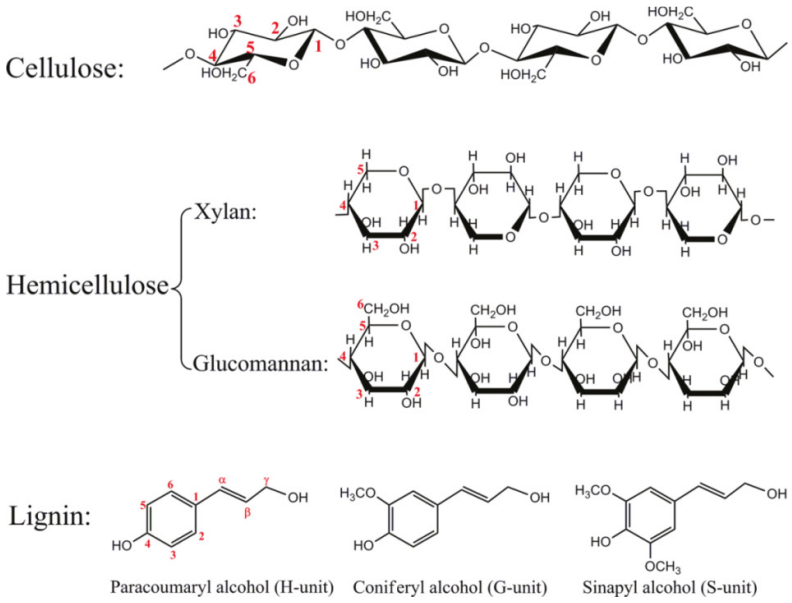


Figure 1 6 Basic Structures of cellulose, hemicelluloses and lignin (Zhang et al., 2011)

1.3.3 Biomass Resources

Biofuels can either be first generation or second generation fuels. First generation biofuels are mainly liquid biofuels and are produced from food crops rich in starch, sugar, animal fats and vegetable oils using conventional technologies. (Naik et al., 2010). The production of these fuels is rather costly due to the inadequate feedstock available and also due to the competition for the crop between food and biofuels. They also effect the biodiversity of the land (Damartzis and Zabaniotou, 2011). On the other hand, second generation biofuels are produced from non-food lignocellulosic crops and are used as solid biomass. These are available in abundance. The conversion technologies for second generation biofuels are still under development but are expected to have lower CO_2 emissions and lower land requirements (Damartzis and Zabaniotou, 2011, Naik et al., 2010).

Some of the potential second generation crops are:

1.3.3.1 Dedicated Energy Crops

Dedicated energy crops are herbaceous and short rotation crops rich in lignocellulosic material that are not grown for food but for other purposes and grow annually or on a 3-10 year cycle to ensure sustainability.

- **Herbaceous energy crops:** These are perennial non-woody rhizomatous grasses like Miscanthus, Switchgrass and Reed canary grass. They undergo C_4 photosynthesis and are usually harvested at the end of the growing season when all the nutrients have translocated back to the roots (Brown, 2003, Karp and Shield, 2008).
- **Short rotation energy crops:** These are woody crops like willow, poplar and eucalyptus using a C_3 photosynthesis pathway and are capable of coppicing. They are usually cut back at the end of the first year to enable the stems to coppice and accelerate their growth. They are usually harvested on a 3-10 year cycle (Brown, 2003, Karp and Shield, 2008).

1.3.3.2 Agricultural and Forestry Residues

Agricultural residues are those excess parts of the plant after the plant has been harvested for food and include shells, hulls, pits, corn stover and many more. Similarly, forestry residues are any parts of the woody stem that are left over after the trees have felled or been trimmed or cut down and include logs, saw dust and many more (Brown, 2003, Jenkins et al., 1998, Loo and Koppejan, 2008).

1.3.3.3 Wastes

Wastes can also be used as biomass to produce energy. They are readily available and are relatively cheap. Using waste as a biomass resource helps to reduce the number of landfill sites needed to dump the waste hence freeing more land to grow food and energy crops. Wastes can be of the following three types:

- **Municipal Solid Waste (MSW)**: This is any general waste that includes paper, plastics, non-flammable materials like glass and steel and food wastes. MSW that is suitable as biomass does not include plastics and non-flammable materials (Brown, 2003, Jenkins et al., 1998).
- **Animal and Human Wastes:** Manure and sewage which are the wastes from animals and humans respectively are also good sources of energy. These are first treated in waste treatment plants and then used to produce heat and electricity (Brown, 2003)
- **Industrial Wastes:** Some of the by-products produced from food processing and cosmetic industries make good sources of energy. Dried Distillers Grains and Solubles (DDGS) produced from the dry grind ethanol process (Morey et al., 2009a) and shea residue, the by-product from producing shea butter (Munir et al., 2009) are some of the examples of industrial wastes.

1.3.4 Biomass Conversion Technologies

Biomass can be converted into energy via bio-chemical and thermo-chemical technologies the former of which produces liquid biofuels for transport while the latter produces hydrogen, bio-oils, heat and electricity. For this study we are

interested in the thermo-chemical conversion technologies. These can primararily be divided into 3 types; combustion, pyrolysis and gasification.

1.3.4.1 Combustion

The reaction of a fuel with oxygen to produce energy is known as direct combustion. This can be done with coal or biomass on their own or by combining the two as a feedstock, which is then called co-firing. The products from combustion are mainly CO_2 and H_2O with traces of NO_x and SO_x. (Naik et al., 2010). For combustion on a large scale, the technologies can be divided as follows:

- **Fluidised Bed Combustion:** Fluidised bed combustion occurs when a suspension of gas and solid bed material (normally silica sand) is introduced into the fluidised bed from the bottom and it aids the fuel to burn. The particle size of the Bubbling Fluidised Bed material (BFB) is 0.5-1mm while that of the Circulating Fluidised Bed is 0.2-0.4mm. Similarly the velocity of the suspension in a BFB is 1-2m/s while that of a CFB is 5-10m/s (Loo and Koppejan, 2008)
- **Fixed Bed Combustion:** In a fixed bed reactor, drying, gasification and combustion of the fuel occurs in primary air. The combustion gases produced are then introduced into a separate chamber along with some more air to burn them off. For biomass combustion, vibrating and rotating grate systems and underfeed stokers are the fixed bed systems that can be used, due to the low ash melting points and high moisture content in biomass (Loo and Koppejan, 2008).
- **Pulverised Fuel Combustion:** This technology is only good for fuels with particle sizes <2mm (Loo and Koppejan, 2008). The fuel and primary air are introduced into the chamber and the combustion of the fuel occurs while it is suspended in air. The introduction of more secondary air helps to burn the combustion gases (Loo and Koppejan, 2008)

1.3.4.2 Gasification

Gasification is the partial oxidation of fuels to produce a gas which contains CO, CO_2, H_2, CH_4 and N_2. This gas can either be syngas or producer gas depending on its composition, the former which can be used to make other fuels while the latter

being used for power generation. Gasification occurs at temperatures as high as 900-1300^{o}C (Naik et al., 2010, Saidur et al., 2011)

1.3.4.3 Pyrolysis

Pyrolysis is the thermo-chemical reaction of biomass in the absence of oxygen to produce char, bio-oil and gases. Depending on the operating conditions pyrolysis can occur in 3 ways; conventional, fast and flash as shown in Table 1.3

Table 1 3 Types of pyrolysis, their operating conditions and their products (S Naik et al 2010)

	Conventional	Fast	Flash
Heating Rate (^{o}C/s)	0.1-1	10-200	>1000
Temperature Range (^{o}C)	277-677	577-977	777-1027
Residence Time (s)	45-550	0.5-10	<0.5
Particle Size (mm)	any	<1	<0.2
Main products	pyrolysis gases and carbon rich residues	Bio-oil, solid chars non-condensed pyrolysis gases	Bio-oil

From all the above technologies, combustion is the most common for heat and electricity generation and co-firing of biomass with coal is of great interest. Co-firing is the third largest renewable electricity generator in the UK (Perry and Rosillo-Calle, 2006)

1.2 Co-firing

Co-firing is the simultaneous combustion of coal and biomass to produce energy and is a very attractive process since it can be easily retrofitted into existing power plants hence reducing further costs of implementing new equipment. It also helps to reduce CO_2, NO_x and SO_x emissions (Perry and Rosillo-Calle, 2006)

Co-firing does have limitations which are discussed here (Loo and Koppejan, 2008).

- Firstly the preparation and handling of the fuel. Biomass cannot be milled as easily as coal due to its fibrous nature and hence the amount and type of biomass co-fired is limited.

- Biomass contains many inorganic constituents like potassium that lowers its ash melting point hence causes slagging and fouling in boilers.
- It can cause combustion related problems such as flame instability and incomplete burnout affecting plant operation.

Optimum co-firing limits depend highly on the type of biomass and coal being used and their mechanical and combustion properties as well as the types of mills, boilers and burners used for the co-firing process. An optimum level would be <15% biomass since tests done at higher levels of 20% caused ash-related problems (Perry and Rosillo-Calle, 2006, Perry and Rosillo-Calle, 2008). Co-firing can be done in 3 ways: (Loo and Koppejan, 2008)

- Direct co-firing: In this case the biomass is fed directly into the coal-firing system. The biomass and coal can be mixed before feeding into the system or there can be two separate feeding systems for the coal and the biomass.
- Indirect co-firing: For indirect co-firing, the biomass is first converted to syngas which is then sometimes cleaned, to remove impurities like alkali and trace metals, tars, condensable organic species and N, Cl and S species, before introducing it into the coal fired system.
- Parallel co-firing: In this case, the biomass is first combusted in a separate boiler and the steam obtained from this is then used in the coal-fired system's steam and power generators.

1.3 Aims and Objectives

The UK imports most of its biomass due to the small availability of indigenous crops. According to the UK Biomass Stratergy 2007, there is potential of developing the biomass supply and creating a sustainable market in the UK which the government intends to facilitate. Better management of woodlands and separate collection of food and wood wastes would help in one way. By offering incentives to increase the production of energy crops and improving the management of these crops would also help increase their supply (DEFRA, 2007).

The major feed stocks imported are wastes from industrial processes such as palm kernels, wood and olive residues (Perry and Rosillo-Calle, 2006) hence one aim of the thesis is to study the combustion properties of some of the imported

feedstocks. In particular, investigation of the behaviour of the ash and its effect on boilers and the emissions of nitrogen and sulphur species from the chars of these fuels is of interest. Fundamental studies of combustion and pyrolysis have also been used on these fuels to characterise their thermal behaviours..

A major aim of this thesis forms part of the UK Supergen Bioenergy Consortium (www.supergen.bioenergy.net) activity. Namely this aim concerns the combustion properties of potential biomass crops for energy production. Here we aim to investigate the effect of agronomy as well as genetic variation on the fuel properties of SRC willow. For these fuels the ash behavior and the ash related problems have been studied. The effects of some of the inorganic constituents on combustion of SRC willow have also been examined.

From the agronomy study, recommendations have been made to the Department for Environmental, Food and Rural Affairs (DEFRA) on how to manage the crops. The genetic study has given an initial conclusion as to how different species of SRC willow can be bred to improve their fuel properties.

1.5.1 Thesis Outline

- **Chapter 1** This chapter looks at an overview of energy demand, supply, security and some of the environmental problems encountered from energy production both globally and in the UK. It also introduces biomass, its resources and some of the thermal conversion technologies.
- **Chapter 2** contains a literature review of some of the fuel properties of biomass and its combustion characteristics.
- **Chapter 3** outlines the fuels analysed for this study, the experimental methods employed for their analyses and the equipment used for the analyses.
- **Chapter 4** presents results of fuel properties of some of the imported feed stocks like olive residue, Palm Kernel Expellers (PKE), shea residue and Dried Distillers Grains and Solubles (DDGS). Their potential for co-firing in UK power plants has been characterised.
- **Chapter 5** examines the agronomy (application of different fertilizer treatments with two sampling times for each year for 3 years) of Short Rotation Coppice (SRC) willow on a small scale. The optimum fertilizer treatment and sampling time for the

best fuel properties have been approximated to assist farmers on improving crop quality and yield.

- **Chapter 6** presents an initial investigation of the fuel properties of different species of SRC willow. This small study helps to identify traits which might be attractive to the next generation of SRC willow. New breeds of willow may offer not just higher yields but also improved fuel properties.
- **Chapter 7** concludes the overall findings from chapters 4 to 6.

Chapter 2

Literature Review

2.1 Introduction

As discussed in Chapter 1, this thesis studies the combustion properties of some imported agricultural residues such as PKE, olive, shea and Dried Distillers Grains and Solubles (DDGS), and the energy crop, Short Rotation Coppice (SRC) Willow. The way in which the fuels have been grown and processed highly influence their chemical composition and hence their behaviour during combustion in furnaces and boilers. For energy crops, the fertiliser regimes and harvest time are vital for optimum fuel properties while, for agricultural residues, the processing technology is the major factor to determine the fuel properties. Crops grown for fuels are most desirable when least cultivation and fertilisation is required, along with low concentrations of certain minerals in the fuel for optimum performance in boilers and furnaces during combustion (Barraclough et al., 2011). Some of the crops are chemically converted into liquid fuels like oil and bioethanol, and the wastes that remain can be used as fuels for heat and electricity generation. This chapter presents a brief overview of the characteristics of biomass in terms of their properties, with particular reference to the properties investigated in this thesis.

2.2 Fuel Characteristics of Biomass

Biomass is chemically composed of proximates, ultimates and mineral content which are discussed in Sections 2.2.1, 2.2.2 and 2.2.3 respectively.

2.2.1 Proximate Parameters

The proximate parameters include moisture, ash, volatile matter and fixed carbon content. The moisture content of different groups of biomass, for example wood and woody biomass or herbaceous and agricultural biomass, contaminated biomass, agricultural biomass is generally higher than that of coal and peat, and can be measured on an as received, air dried or oven dried basis with air dried being the most common. Their moisture contents vary from approximately 3-63% straight from harvesting but have a narrower range when they are air dried (1-20%). The ash

content of biomass varies between 0.1- 46% on a dry basis and is generally lower than that of coal and peat which have ash contents between 4 and 52%. Volatile matter and fixed carbon contents on a dry basis of the different groups of biomass vary between 48-86% and 1-38% respectively while that of coal and peat vary between 12-68% and 20-72% respectively (Vassilev et al., 2010).

2.2.2 Ultimate Parameters

The ultimate parameters are weight percent carbon (C), hydrogen (H), nitrogen (N), sulphur (S), chlorine (Cl) and oxygen (O). For biomass, O constitutes approximately 30-40 wt% dry matter due to its high cellulose content while C constitutes 30-60 wt% and H makes up 5-6 wt% dry matter. N, S and Cl are present in minute quantities of <1 wt% dry matter (Jenkins et al., 1998) although the N and S contents might exceed 1% in some cases such as in agricultural residues (Darvell et al., 2010, Gudka et al., 2012). Fuels with high N and S contents emit the pollutants NO_x and SO_x during combustion and this is discussed further in Section 2.4.2. Figure 2.1 illustrates a coalification diagram from which the relationship between the H:C and O:C ratios of coal to different types of solid fuels can be understood and estimated boundaries between the fuels can be identified.

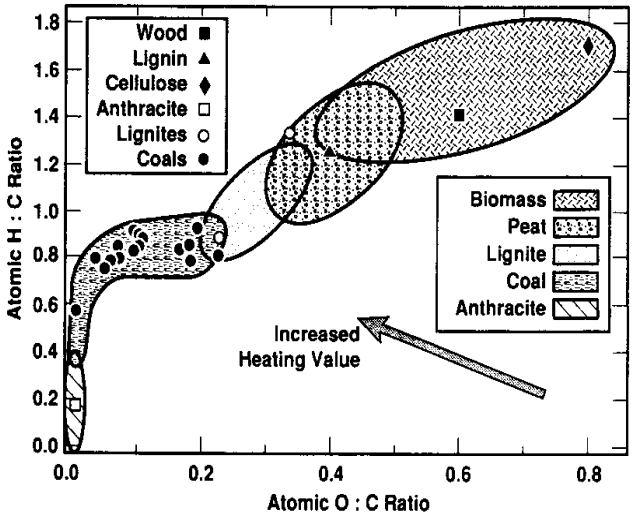


Figure 2 1 Coalification diagram showing the relationship of different types of solid fuels in terms of their chemical compositions (Baxter, 1993).

The H/C and O/C ratios influence the amount of fuel lost during pyrolysis. As the H/C and O/C ratios increase, the fuel becomes less aromatic hence making it easier to decompose during pyrolysis (Baxter, 1993, Jenkins et al., 1998). H/C and O/C also correlates with the calorific value of the fuel; this decreases as we move left to right on the coalification diagram (Jenkins et al., 1998).

2.2.3 Mineral Content

Biomass contains minerals composed of inorganics, including K, Ca, Mg, Na, Fe, Al, Si, Ti, Mn, P, S and Cl. These influence the ash chemistry behaviour in combustion. Other metals such as Cu, Co, Cr and Pb are present in trace amounts, but can be important because of their potential emission from the stack (Jenkins et al., 1998). The minerals are present mainly as oxides in the biomass ash after combustion.

- Potassium is abundant in agricultural grasses and straws and plays a key role in regulating the osmotic potentials across membranes and in the cytoplasm, regulating the stomata, activating enzymes and transporting membrane which is the reason why it is found in plant parts with highest growth. It is present in the form of a mobile, univalent ion (K^+) with little structure. The metabolic activity of the plant influences its uptake from the soil (Bryers, 1996).
- Calcium is responsible for the structure and the growth of the plant. Exchangeable bonds with the cell wall are formed by calcium and it plays a key role in forming a rigid wall (Bryers, 1996).
- Sulphur in plants is in the form of sulphates which increase as the sulphur in the fertilizers increase. Plants also contain organic sulphur which is less sensitive to fertilizer sulphur (Bryers, 1996).
- Aluminium contents in plants are mostly toxic and their presence in quantities >300ppm indicates that the plant has been tainted with soil or dirt (Bryers, 1996).
- Silicon contents in plants are approximately 0.1-10% on a dry basis and are absorbed from the soil as silicic acid. It is mostly deposited in the amorphous form but seldom in crystalline form of a hydrated oxide SiO_2. nH_2O (Bryers, 1996).

- Iron is mainly found in the leaves of plants. It plays a key role in the reversible reactions of photosynthesis and respiration and it also forms chelates that are active in transport of nutrients. (Bryers, 1996).

During combustion, a fuel with low moisture, ash and mineral contents is favourable since these if present in high amounts cause problems in boilers and furnaces. High moisture contents are undesirable since excess energy would be required to drive of the moisture from a sample before combusting it (ie lowers the recoverable heat). The minerals in the fuel form oxides when burnt and these are present in the ash which can cause slagging, fouling and corrosion in boilers therby reducing their efficiency. This is discussed further in Section 2.4.1. These obstacles may be overcome in part by utilising appropriate means to produce the fuel.

2.3 Agronomy of Energy Crops

2.3.1 Fertilizer Application

The main macronutrients required for the growth of good quality crops are nitrogen (N), potassium (K) and phosphorous (P). The application of these fertilizers may alter the chemical composition of the crops. Previous studies examined the effect of nitrogen fertiliser on fuel properties for certain energy crops such as miscanthus, reed canary grass and switchgrass as well as some winter crops like rye, triticale and wheat (Lewandowski and Kauter, 2003) have concluded that an increase in nitrogen fertiliser leads to an improved crop yield but poorer fuel quality. The uptake of nitrogen fertiliser also increases uptake of certain minerals especially K and Mg which deteriorates the ash behaviour during combustion of the crops. An increase in uptake of organic metal from the soil due to high N concentrations is known as ion synergism, i.e. the uptake of an ion by another kind of ion; and the plant cells reach electrostatical balance between cations and anions using ion synergism (Lewandowski and Kauter, 2003). High levels of nitrogen fertiliser also improve the growth of roots hence increasing the root surface available for nutrients uptake from the soil (Barraclough et al., 2011, Lewandowski and Kauter, 2003).

2.3.2 Harvest Time

The harvest time of the crop is very important as it has a major influence on the fuel properties. It has been reported previously that the optimum time for harvesting energy crops like reed canary grass, switchgrass and Miscanthus in terms of fuel properties is winter but there is the disadvantage of lower yields at this time. By winter, the leaves have fallen, and the crop has senesced and, as a result, the yields are lower than when harvested in late summer or autumn. The low moisture, ash and mineral contents which are achieved in winter make the crops more suitable for use in boilers and furnaces. Some of the minerals like P and N from the plants translocate into the soil by winter and are stored there for the growth of crops during the following year. Hence this approach to crop management reduces the amount of fertiliser application required for the following year's crop. In addition other minerals like K and Mg are leached out and so also present in lower amounts in a winter harvested crop. During a late harvest, the N and S contents of the crop are low hence the NO_x and SO_x emissions are reduced during combustion (Barraclough et al., 2011, Ogden et al., 2010).

2.3.3 Short Rotation Coppice (SRC) Willow

SRC willow is a fast growing woody biomass that is grown as short rotation coppice and undergoes the C_3 photosynthesis pathway (McKendry, 2002). When the plant is dormant in the winter, its stem is cut very close to ground level allowing multiple stems to grow in the following year and this is known as coppice. It is usually harvested every 3 years and normal yields are between 12-15 oven dry tonnes per hectare (DEFRA, 2004). Figure 2.2 shows a typical willow plantation in the UK.

Figure 2 2 SRC willow trial in Bawtry

The ability of the SRC willow root system to absorb large amounts of trace metals helps to remediate contaminated land and sewage sludge. The nutrient requirement for SRC willow is minimal since it has the ability to store nutrients in the woody part when they are not required. As a result during senescemse, the nutrients from the leaves and stems translocate to the woody parts of the willow until they are required in the next growing season (Ericsson, 1994, Jensen et al., 2009).

2.4 Biomass Combustion

Biomass combustion takes place in four stages as illustrated in Figure 2.3. The duration of each of the four stages depends on the size and shape of the particle. Larger particles take longer to burn compared to smaller particles. For example a study conducted by (Jones et al., 2007) revealed the duration of the four stages for raw SRC willow with particle sizes between 0.05-4mm, which are reported in Figure 2.3. For the willow particles, the volatile and char combustion seem to overlap. For entrained particles, these time scales would be shorter.

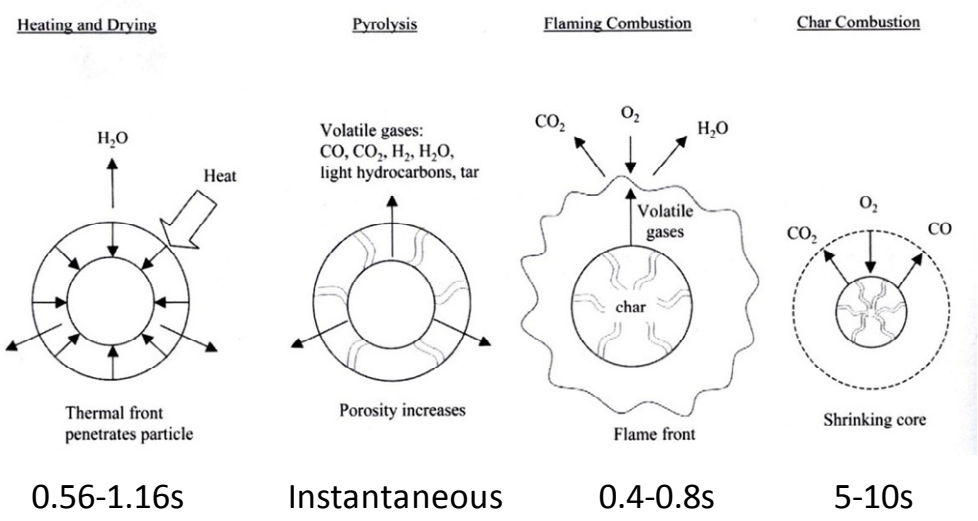


Figure 2 3 Range of time scales for the 4 stages of combustion in biomass for particles between 0.05 and 4mm (Brown, 2003, Jones et al., 2007)

- **Heating and Drying:** First, the fuel particle starts to *heat* up and *drying* occurs since a wet sample will prevent the temperature from rising and inhibit pyrolysis (Brown, 2003).
- **Pyrolysis:** During *pyrolysis,* the organic compounds in the fuel particle start to decompose and CO, CO_2 and CH_4 along with other heavy molecular weight compounds are released from the fuel. These volatiles do not oxidise immediately since the availability of oxygen is low due to the huge amount of gases flowing from the surface of the fuel. The release of volatiles makes the fuel porous forming a carbon rich residue called char (Brown, 2003). Biomass has a higher volatile matter content compared to char while the opposite is true for coal.
- **Flaming Combustion:** In the third step the volatile gases have dispersed from the surface of the particle to the air, where sufficient oxygen is available for their combustion and CO_2 and H_2O are the products formed. In cases where sufficient oxygen is not available, toxic compounds like CO, polycyclic hydrocarbons (PAHs) and furans are produced. High chlorine fuels can also form dioxins. *Flaming combustion* occurs and an orange flame is seen during volatile combustion which is due to the presence of soot (Brown, 2003).
- **Char Combustion:** In the final step, *char combustion* occurs. If oxygen reacts with the char on the surface of the fuel particle, then shrinkage is seen at the core of the

char. Conversely, if the oxygen penetrates into the char then the fuel particle becomes more porous as combustion progresses. The final residue remaining after complete combustion is known as ash. The char contains some mineral matter which oxidises during char combustion and the corresponding mineral oxides are retained in the ash (Brown, 2003).

2.4.1 Ash Related Problems of Biomass

Two types of ashes are produced during biomass combustion; bottom ash and fly ash.

- **Bottom Ash** is the solid residue that is not entrained in the flue gases but exits at the bottom of the furnace.
- **Fly Ash** on the other hand are the fine particles of the ash that rise with flue gases, and exit via the top of the furnace through the heat exchangers.

Biomass ash is mainly composed of K_2O, Na_2O, CaO, MgO, Fe_2O_3, TiO_2, Al_2O_3, SiO_2 and P_2O_5, SO_3 and Cl. The alkali metals, K and Na, play a major role in ash deposition in biomass and coal fired power plants respectively (Baxter et al., 1998). These alkali metals react with chlorine, sulphur and silicon to produce gaseous and molten products which deposit on refractory walls and superheater and re-heater regions. Three forms of ash deposition can occur during combustion; slagging, fouling and corrosion, which reduce efficiency of the system and effect the lifetime of plant components.

2.4.1.1 Slagging

During biomass combustion, alkaline earth metals and alkali metals, mainly K, react with silicon and sulphur to produce molten potassium silicates ($K_2Si_4O_9$) and aluminosilicates ($KAlSi_2O_6$) as well as gaseous potassium sulphate (K_2SO_4). These molten particles and vapours may then impinge directly onto the heat transfer surfaces in the combustion zone to form a glassy layer called slag. Slag usually builds up on grates while running slag has a tendency to accumulate on high temperature refractory walls and water walls and it is present in rock-like, ribbon-like and hair-like structures. Slag formation starts with a thin layer of fly ash being

deposited on the refractory walls which slowly builds up with adequate thermal resistance creating more sticky surfaces for ash particles to be captured on. This increases the size of the deposit layer (Baxter et al., 1998, Bryers, 1996, Wei et al., 2005)

Figure 2 4 Slagging in a Furnace

2.4.1.2 Fouling

Fouling occurs when a layer of unwanted deposits is formed on heat transfer surfaces (Lewandowski and Kicherer, 1997). Alkali chlorides, sulphates and hydroxides in the flue gas condense on the superheater regions forming a deposit layer. The initial layer contains alkali matter and the fly ash that contains alkali chlorides and sulphates stick on to these deposits. The alkali chlorides may react with sulphur in the flue gas to form alkali sulphates which is the more favoured reaction. Just like slag, these deposits have low melting points hence increasing the sticky surfaces for more deposition (Bryers, 1996, Davidsson et al., 2006).

Figure 2 5 Fouling on Heat Exchangers

2.4.1.3 Corrosion

Corrosion is the reaction of metal surfaces with unwanted deposits which gradually attack the equipment which in turn increases maintenance costs (Lewandowski and Kicherer, 1997). A dominant corrosion reaction with many biomass fuels, particularly straws involves chlorine. The alkali chlorides which deposit on the refractory walls and superheaters, react with the iron (Fe) on the equipment and form iron chlorides which corrode the equipment (Baxter et al., 1998, Khalil et al., 2011).

Figure 2 6 Corrosion on biomass superheater tube

2.4.2 Pollutants from Biomass Combustion

During the combustion of biomass, the N and S in the fuel oxidise to produce NO_x, N_2O and SO_x emissions. NO_x (NO and NO_2) plays a role in the formation of acid rain and photochemical smog, while N_2O is a potent greenhouse gas (Ren et al., 2011). Sulphur oxides (SO_x) on the other hand can be harmful on the human respiratory system and also causes acid rain.

2.4.2.1 NO_x

NO_x emissions can be formed via the thermal or prompt mechanism or via the combustion of fuel bound nitrogen.

- **Thermal NO_x** is formed by the fixation of nitrogen in the combustion air at temperatures above 1800 K. NO can be formed via the following reactions (Glarborg et al., 2003):

$$O + N_2 \leftrightarrow NO + N \qquad \text{Equation 2.1}$$

$$N + O_2 \leftrightarrow NO + O \qquad \text{Equation 2.2}$$

$$N + OH \leftrightarrow NO + H \qquad \text{Equation 2.3}$$

- **Prompt NO_x** is formed when a CH radical attacks the triple bond in a nitrogen molecule (N_2) as in Equation 2.4

$$CH + N_2 \leftrightarrow NCN + H \qquad \text{Equation 2.4}$$

The NCN would then be oxidised to NO or revert back to N_2 (Glarborg et al., 2003).

- **Fuel NO_x** is formed during the oxidation of fuel bound nitrogen and it is the key source of NO_x along with minor amounts of thermal NO_x in the combustion process (Glarborg et al., 2003). The reactions occurring during NO_x formation are illustrated in Figure 2.7 (Williams et al., 2012) and described below.

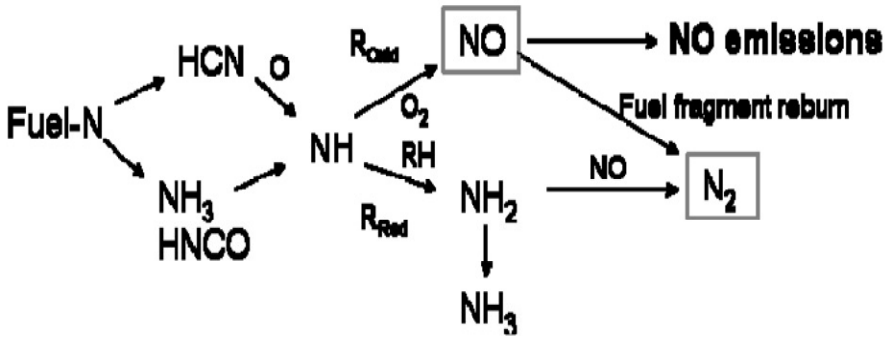


Figure 2 7 NO_x formation pathways from fuel nitrogen (Williams et al., 2012)

Fuel NO_x Mechanisms

The nitrogen content in biomass is generally lower than that of coals. During the combustion process, the fuel bound nitrogen is split between the volatiles and the char and this split is highly influenced by the structure of the fuel and the temperatures (Glarborg et al., 2003, Hansson et al., 2004). Nitrogen in biomass is mainly in the form of proteins while nitrogen in bituminous (and high rank) coal exists in the form of pyrrolic (five ring), pyridinic (six ring) and quaternary nitrogen. As the oxygen content of the fuel increases, i.e in low rank coals and biomass, the fraction of nitrogen released with volatiles increases. At low temperatures (600-1200K), the amount of nitrogen retained in the char for low rank coals and biomass is greater than that for bituminous and high rank coals while at higher temperatures

(850-900K), biomass releases more nitrogen (up to 80%) with the volatiles. (Glarborg et al., 2003).

Volatile Nitrogen Species

During the devolatilisation of solid fuels at high temperatures (above 1300K), the amine groups are cleared and the ring structure of the pyrrolic and pyridinic structures of the fuels open up and NO_x and N_2O precursors like hydrogen cyanide (HCN) in coals and, ammonia (NH_3) and cyanaric acid (HCNO) in low rank coals and biomass are produced (Glarborg et al., 2003, Ren et al., 2011). In the presence of an oxygen functionality group like carboxyl or hydroxyl, NH_3 is a potential product. At temperatures between 900 and 1300K, NH_3 and HCNO are the main products for biomass and low rank coals ((Hansson et al., 2004) and above this temperature, HCN is the main gaseous product. The NH_3 and HCNO then oxidise to form NO and in another reaction (not illustrated in Figure 2.7), the HCNO reacts with NO to form N_2O as in Equation 2.5 at temperatures similar to those of fluidised bed combustion (Glarborg et al., 2003).

$$NCO + NO \leftrightarrow N_2O + CO \qquad \text{Equation 2.5}$$

Low-NO_x burners and other firing strategies can help reduce the amount of NO_x formed during volatile combustion, but nitrogen oxides released during char combustion are more difficult to control. Low NO_x burners can reduce NO back to N_2 by keeping the stoichiometry fuel rich in the devolatilisation zone (Glarborg et al., 2003).

Char Nitrogen Species

During char combustion, the char nitrogen reacts with oxygen to produce NO. As the amount of char increases, the particle size increases, and the conversion efficiency of fuel-N to NO decreases since some of the NO in the pores of the char reduces to N_2 by reaction with carbon. This is because the residence time of the NO in the char is longer hence allowing sufficient time for its reduction to N_2. Very little HCN and minute quantities of HCNO are produced during char combustion at temperatures <1100K N_2O is also formed during char combustion via a homogenous

or heterogenous reaction. In the homogenous reaction, the NCO radical reacts with NO to produce (Glarborg et al., 2003) N_2O while in the heterogenous reaction, some of the char nitrogen is oxidised to produce NCO which then follows the homogenous reaction (Glarborg et al., 2003). N_2O can also form from the combustion of oxygenated chars (Jones et al., 2004) The NO-CO reaction becomes an important route. At high temperatures the carbon in the char forms CO which reacts with NO and is catalysed by the carbon in the char (Glarborg et al., 2003, Jones et al., 1995, Ren et al., 2011).

2.4.2.2 SO_x

Mechanisms of sulphur emissions from coal and biomass during combustion have received less attention in the literature. Both organic and inorganic sulphur are present in biomass. The S in coal is mainly in the form of mercaptans. (Li et al., 2009) studied the S functionalities of coal and sewage sludge both individually and during co-combustion, and showed that both sewage sludge and coal had similar S functionalities but their transformation tendencies are different . SO_2 is the major product in the presence of abundant air while S_2, H_2S, OCS, SH, CS and SO_2 are the products of a fuel-rich flame. During combustion of coal, OCS is a product which may be formed due to the partial oxidation of organic sulphur or by the reaction of SO_2 with char sulphur (Jones et al., 1995).

2.5 Physical Properties of Biomass

The physical properties of a fuel are also very important as they affect the handling of the fuel in terms of transportation, storage and also when it is fed into the boiler.

2.5.1 Grindabillity of biomass fuels

When co-firing coal with biomass, the fuels need to be pulverised before combusting them in the boiler. Fuels are milled in power stations for two main reasons:

I. In power stations into fine particles that can be easily fed into boilers and,

II. In pellet production in order to increase bulk density and make transportation and storage of the fuels easier.

The fibrous structure of biomass consisting of the lignocellulosic components; cellulose, hemicellulose and lignin imposes limitations and very high energy penalties on reducing its particle size. During the milling of biomass, it has been found that particles containing any lignocellulosic material do not grind as well as particles containing proteins, lipids and soluble carbohydrates only (Bridgeman et al., 2007).

The grindability of a fuel is the relative ease with which the particle size of a fuel can be reduced and for coal this is often measured using the Hardgrove Grindability Index (Agus and Waters, 1971). Fuels which have high values of HGI can be ground with more ease compared to those with low HGIs and this means that they require less energy for the milling process.

In order to improve the grindability of biomass fuels, pre-treatment methods like torrefraction are being studied intensively. A study done by Bridgeman et al to show the grindability of raw and torrefied Miscanthus and willow samples using a ball mill concluded that compared to four reference coals with known HGIs, the raw Miscanthus and willow were very difficult to pulverise. On the other hand the willow samples need to be torrefied at high temperatures (290^{o}C) and for longer residence times (60 mins) while Miscanthus samples need to be torrefied at the same temperature with short residence times (10 mins) in order to obtain grindability results similar to those of coal (Bridgeman et al., 2010). Figure 2.8 shows an example of particle size distribution of the reference coals, raw willow and torrefied willow after it was milled using a ball mill. Willows A-D represent increasingly severe torrefaction conditions.

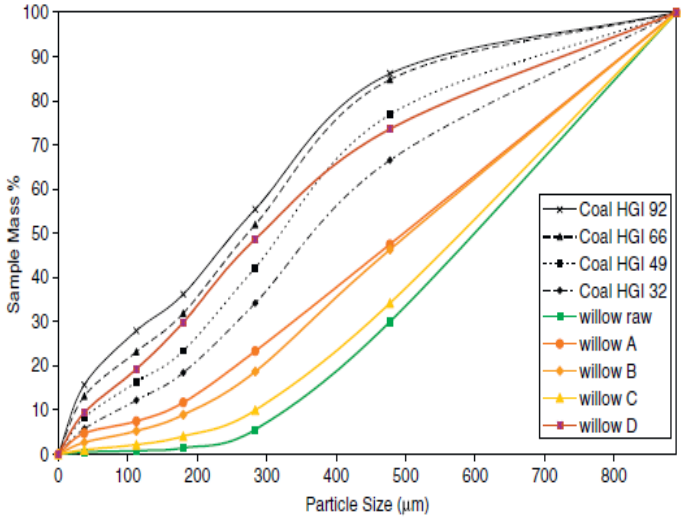


Figure 2 8 Particle size distribution of four different coals of known HGIs, raw willow, and willow torrefied under four different conditions.

Different biomass contain different lignocellulosic composition, and it is possible that their propensity for milling also varies. Chapter 6 will examine the grindability of different genotypes of willow in order to explore their variability.

Chapter 3

Materials, Experimental Methods and Equipment

3.1: Introduction

This chapter describes the biomass materials that have been characterised for their different fuel properties. The methods and equipment used for the characterisation have also been described.

3.2: Materials

Biomass can be categorised according to the techniques that are used for its conversion. Agricultural biomass like wood and woody material and herbaceous and annually growing material like grasses and straws can be burned directly. Direct combustion can also be applied to agricultural wastes like shells, husks, pits and animal manures and solid wastes like non-recyclable paper. Starchy crops like corn and sugarcane can be fermented to produce ethanol which is a liquid fuel. Biodegradable waste can be anaerobically digested using bacteria and fungi producing methane for the production of heat and electricity (Jenkins et al., 1998, McKendry, 2002, Demirbas et al., 2009).

Fuel characterisation of some imported biomass feedstocks like olive residues, Palm Kernel Expellers (PKE), shea residue, Dried Dustillers Grains and Solubles (DDGS) from wheat and Short Rotation Coppice (SRC) willow has been investigated for this study to look at how these fuels can be co-fired with coal in power stations to produce heat and electricity.

3.2.1: Olive Residue

The solid residue that remains after the extraction of olive oil is known as the olive residue. Olive oil can be produced using different extraction systems which may include the traditional two-phase discontinuous pressing system or the modern three-phase continuous centrifugation system. Italy, Spain, Greece and Portugal produce almost 75% of the world's olive oil and hence generate a lot of olive waste (Encinar et al., 2009). Most of the olive waste used for co-firing in the UK is imported from Italy, Spain and Greece (UK Biomass Strategy, May 2007). Three

olive residues, A, B and C, (shown in Figure 3.1) from different suppliers used for this study were provided by RWE npower. Residues A and C were pulverised fuels while B was in the form of pellets but had to be milled in order to carry out the analysis.

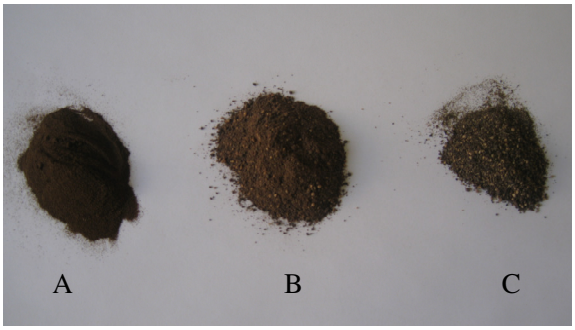


Figure 3 1 Olive Residues A, B and C

3.2.2 Palm Kernel Expellers (PKE)

The by-product produced when a palm kernel is crushed and the oil from it is expelled is called PKE. The high protein and fibre content as well as high energy value of PKE makes it suitable to be used both as an animal feed and for energy purposes (Perry and Rosillo-Calle, 2008). Currently the world's largest producer and exporter of palm oil is Malaysia (Idris et al., 2010). All the palm residues that are co-fired in the UK are imported from Malaysia and Indonesia (UK Biomass Strategy, May 2007). The PKE studied here which is shown in Figure 3.2 was supplied by RWE npower in a pulverised form.

Figure 3 2 PKE Residue

3.2.3: Shea Residue

The fleshy mesocarp shell and husk that remain after the removal of fatty butter from the nut of the shea tree is known as the shea residue. (Munir et al., 2009) The main producers in the world of Shea butter are the West African countries. The shea residue co-fired in the UK is imported from Africa (UK Biomass Strategy, May 2007). The shea residue in Figure 3.3 was provided by RWE npower.

Figure 3 3 Shea Residue

3.2.4: Dried Distillers Grains and Solubles (DDGS)

DDGS is a residue produced by mixing by-products from the dry grind ethanol process namely, Distiller's Wet Grains (DWG) and concentrated distillers soluble in varying proportions and drying it (Morey et al., 2009b). Due to its high protein and fibre contents, DDGS is used exclusively as an animal feed but it also has the potential to produce heat and power and can be used for co-firing (Giuntoli et al., 2009, Morey et al., 2009b). DDGS produced from wheat at a distillery in France was supplied by Cranfield University in the form of pellets. The sample was ground using a Retsch cutting mill SM 100 as shown in Figure 3.4 to a particle size ~600 µm and analysis was conducted on this sample.

Figure 3 4 DDGS Residue

3.2.5: Short Rotation Coppice (SRC) Willow

Willow is a deciduous tree or shrub of the genus salix consisting of strong lightweight wood and narrow leaves. SRC willow is a dense plantation of different varieties of willow which produce high yields and are harvested on 2 to 5 (mostly 3) year cycle (DEFRA, 2004). SRC willow requires macronutrients like N, P and K for healthy growth. Rothamstead Research (Department of Plant and Invertebrate Ecology, Rothamsted Research, Harpenden, Herts, AL5 2JQ, UK), conducted a trial experiment to see the effect of different fertilizer treatments and harvest times on the yields of SRC willow and samples from this trial were analysed at Leeds for their fuel characteristics. Details of the trial are presented in the next section. Rothamsted Research also captured different species of willow in the National Willow Collection (NWC) and these were also analysed at Leeds for fuel characteristics.

3.2.5.1: Agronomy

Short Rotation Coppice willow of the genotype *S.olof* was planted in 2006 at Coppice Resources Ltd, Retford as shown in Figure 3.5. After first year cut back, 15 different fertilizer treatments were applied as part of the larger fully replicated field trial (three replicates for each treatment in randomized blocks). The field trial setup is shown in Appendix A. The fertilizer was applied in two doses, the first dose was applied on 04/04/2007 and the 2nd dose was applied on 10/05/2007. The crop was sampled biannually for three years in autumn and spring. At each sampling time, the stems of 3 stools were cut above the coppice, which in turn was cut from a designated sampling area within the plot. Each sample was taken at least 1 metre away from the previous samplings. The stools were weighed and 10 stems were sub-sampled. The range of length of row that the 3 stools were taken from was 50 centimeters to 2 meters. The stems were then chipped and dried at 80^{o}C for 36 hours before milling and sieving them to a particle size of <600µm. These were then stored in air tight containers. The autumn sampling was carried out before the crop had lost its leaves and the sampled material was split into leaves and stems. In the spring only buds were present on the stems and branches and these were included in the stem material. From the 15 fertilizer treatments, 6 treatments were selected for

this study. The different fertilizer treatments and the sampling dates are listed in the Table 3.1 and 3.2 respectively.

Figure 3 5 SRC Willow Agronomy Trial at Bawtry

Table 3 1 Fertilizer Treatments applied to SRC Willow

Treatment	Fertiliser application per hectare (single plot area 6 x 10.5 m)
A	0 Kg N as $NH_4(NO_3)$
D	150 Kg N as $NH_4(NO_3)$
F	250 Kg N as $NH_4(NO_3)$
J	100 Kg K as K_2O + 150 Kg N $NH_4(NO_3)$
N	80 Kg SO_3 as $(NH_4)_2SO_4$ balanced to give 150 Kg N as $NH_4(NO_3)$
O	Sewage pellets

Table 3 2 Sampling dates for the 3 years of SRC Willow

Year	Autumn Leaves and Stems	Spring Stems
1 (2007-2008)	15/10/2007 (1st sample)	11/03/2008 (2nd sample)
2 (2008-2009)	30/09/2008 (3rd sample)	10/03/2009 (4th sample)
3 (2009-2010)	12/10/2009 (5th sample)	18/01/2010 (final harvest)

3.2.5.2: Genetics

Short Rotation Coppice Willow was grown in the National Willow Collection (NWC) at Rothamsted Research as shown in Figure 3.6. Different species of salix obtained from different countries around the world were captured in the NWC. 99 accessions were then sampled. From these 99 samples, 6 samples which contained the lowest and highest cellulose, hemicelluloses and lignin contents were selected to

analyse for their fuel characteristics. These were *S. drummondiana Barratt ex Hook, S.eriocephala Michx, S.aurita L, S.mielichhoferii Saut, S.viminalis x S.schwerinii* and *S.elaeagnos Scop* Table 3.3 shows the different genotypes with varying biochemical compositions. The genetic samples were not replicated and no fertilizer treatment had been applied to these samples. 1 stool was randomly taken from a central 6 stools in each plot. The branches of each stool were cut above the coppice cut and these were then chipped and dried at 80^{o}C for 36 hours before milling and sieving them to a particle size of <600µm. These were then stored in air tight containers. The first set of genetic samples was taken in December 2008. The crop was sampled again in February 2011 for the 6 genotypes with the varying biochemical composition. The genotype samples only included stems.

Figure 3 6 National Willow Collection at Rothamsted Research

Table 3 3 Genotypes of SRC Willow with varying biochemical composition

Genotype	Lowest	Highest
S. drummondiana Barratt ex Hook	Cellulose	
S.eriocephala Michx		Cellulose
S.aurita L	Hemicellulose	
S.mielichhoferii Saut		Hemicellulose
S.viminalis x S.schwerinii	Lignin	
S.elaeagnos Scop		Lignin

3.3: Experimental Methods

3.3.1 Proximate Analysis

The proximate analysis includes the moisture, ash, volatile matter and fixed carbon content of the fuel and these were all conducted according to the British Standard methods. The moisture content was determined in accordance with DD

CEN/TS 14774-3: 2004 in which 1g of sample was dried in a Carbolite MFS oven in the presence of nitrogen until constant mass was achieved. To determine the ash content according to DD CEN/TS 14775:2004, 1g of sample was slowly combusted in a Carbolite OAF 101 Furnace at a temperature of 250^{o}C for one hour and then the temperature was raised to 550^{o}C for 3 hours until there was no further mass loss. For determining the volatile content according to DD CEN/TS 15148:2005, 1g of sample was introduced into a Carbolite OAF 101 furnace which was preheated at 900^{o}C for 7 minutes. Finally the fixed carbon content was calculated by difference using Equation 3.1.

Fixed Carbon = 100 - % Moisture- % Ash - % Volatile Matter (Equation 3.1)

3.3.2: Ultimate Analysis

The C, H, N and S values were determined by flash combustion using a Thermo Instruments Flash EA 1112 Series. Measurements were done as a weight percentage. All measurements were done in duplicates and corrected for moisture, and a mean value is reported. The chlorine (Cl) measurements were carried out at Rothamsted Research as in section 3.3.2.1.

3.3.2.1: Chlorine Content

The chlorine content (conducted by Rothamsted Research) was measured by continuous flow colourimetric analysis. Plant material was first dried at 80^{o}C for 4 hours and cooled in a dessicator. 0.5 gram of the sample was weighed into a polythene bottle. The chloride was then extracted from the plant material by shaking with cold water and filtering the extract into a Sterilin vial through a Whatman no.40 filter paper. The filtered solutions were analysed for chloride content by the Skalar SAN^{PLUS} System.

The oxygen (O) content was calculated by difference using Equation 3.2.

% O = 100 - % C - % H -% N -% S -% Cl (Equation 3.2)

3.3.3: Calorific Value determination

The calorific value was calculated using the C, H and N values determined in section 3.3.2 on a dry basis. "Friedi et al" provided two calculations which are based on the C, H and N content of dry biomass; an ordinary least square regression (OLS) and a partially least square regression (PLS) method as in Equations 3.3 and 3.4 respectively.. These were calibrated using 122 different biomass samples and provide the energy content of fuels on a dry basis. (Friedl et al., 2005)

$$HHV(OLS\ model) = 1.87C^2 - 144C - 2820H + 63.8C \times H + 129N + 20147$$

(Equation 3.3)

$$HHV(PLS\ model) = 5.22C^2 - 319C - 1647H + 38.6C \times H + 133N + 21028$$

(Equation 3.4)

Since both models have almost the same performance it was deemed appropriate to use an average of both and a final model for high heating value (HHV) prediction was obtained. (Equation 3.5)

$$HHV = 3.55C^2 - 232C - 2230H + 51.2C \text{ X } H + 131N + 20{,}600 \quad \text{(Equation 3.5)}$$

This equation yields the HHV on a dry basis in units of MJ/kg.

3.3.4: Biochemical Composition

The biochemical composition of the larger data sets which include the SRC willow agronomy experiment and the 99 samples from the National Willow Collection was estimated as described in Section 3.3.4.1 while that of the 6 genetic samples which were sampled at a later date from the NWC and the DDGS were determined using wet chemical methods as in Section 3.3.4.2.

3.3.4.1: Estimation of cell wall composition

Determination of cell wall composition was conducted as part of the research programme at the Institute of Biological, Environmental and Rural Sciences (IBERS) within the Supergen Bioenergy Consortium. This method has been published (Allison et al., 2010) and a description of the method is summarised here. A NIR (near infrared spectrometry) Systems model 6500 near-infrared scanning

monochromator (FOSS NIR Systems Inc., Laurel, MD) was used to scan dried and ground samples in small ring cups of 36 mm diameter. An average of 32 successive scans of the sample was made over the wavelength range from 400 to 2498 nm at 2 nm intervals using WinISI II 1.04a (Infrasoft International LLC, State College, PA) software. Specific models were used to predict the cell wall composition of the samples. Samples representative of the population were selected based on Mahalanobis H (Global H) and neighbourhood H (NH) distances using a NH distance of 1.0 (Shenk, 1991a, Shenk, 1991b). During calibration development spectral data from 1100–2498 nm was use0d with each sample having a total of 700 data points. Calibration models for Neutral Detergent Fibre (NDF), Acid Detergent Fibre (ADF) and Acid Detergent Lignin (ADL) were developed by a modified partial least squares approach as described elsewhere (Sanderson, 1997) using standard normal variate and de-trending transformations (Barnes, 1989). Model development included cross validation (eight groups) to avoid over-fitting and to assess model robustness. The final equations were selected on the basis of minimal standard error of cross validation (SECV) and maximal coefficient of determination of cross-validation (R^2_{CV}).

3.3.4.2: Analytical determination of ADL, ADF and NDF

Gravimetric measurements of NDF, ADF and ADL were made (at IBERS) using refined versions of Van Soest's methods (Van Soest, 1963) using the Gerhardt fibrecap system. Briefly, NDF, which is regarded as total cell wall, is the residue, corrected for ash, left after refluxing for 1 h in a neutral buffered detergent solution. ADF, the ash corrected residue remaining after refluxing the samples in a solution of Cetyl Ammonium Bromide (CTAB) in 2 M sulphuric acid is a measure of cellulose and lignin only. ADL was measured by treating ADF with 72% sulphuric acid to solublise the cellulose to determine crude lignin. Ash was determined in the samples after heating at 600˚C in a muffle furnace for at least 4 h. The concentration of hemicelluloses and cellulose were calculated according to Equations 3.6 and 3.7 respectively.

% Hemicellulose = % NDF - % ADF (Equation 3.6)

% Cellulose = % ADF - % ADL (Equation 3.7)

3.3.5: Grindability Tests

The British Standard for Hardgrove Grindability Index (HGI) BS 1016-112:1995 can be used for coal but not biomass. Since the volumes of the specified 50g differ between greatly between biomass and coal, and since this would result in different grinding conditions, the method was modified to give an "Equivalent HGI", HGI_{eqiv}. The modified method involves using a fixed volume of biomass or coal sample (50 cm^3) instead of having a fixed mass (50g). (Agus and Waters, 1971, Joshi, 1979, Bridgeman et al., 2010). These tests were done to see how the different genotypes of SRC willow grind compared to each other and to some standard coals.

3.3.5.1: Volumetric Hardgrove Grindability Index (HGI) tests

Dried samples, milled using a blade cutting mill, were sieved through a 1.18 mm and a 600 µm sieve. 50 cm^3 of sample with an accuracy of ± 0.1 cm^3 from the fraction retained on the 600 µm sieve was measured and weighed. The weighed sample was then placed in a 250 ml capacity stainless steel milling cup along with 15 x 20 mm stainless steel balls shown in Figure 3.7a and ground in a Retsch PM100 ball mill shown in Figure 3.7b for 2 minutes at 165 rpm. The sample was then removed from the grinding cup and sieved using a 75µm sieve in a mechanical shaker and the two fractions were then weighed to the nearest 0.01 g. Losses of weight loss > 0.5 g led to repeating the test. The mass of sample passing through the 75µm sieve was calculated as in Equation 3.8

$$m = m_v - m_1 \qquad \text{Equation 3.8}$$

where m_v is the mass of 50 cm^3 sample and m_1 is the mass of sample that remains on the 75µm sieve. Each sample was tested in duplicate and an average value is reported. 4 reference coals with known HGIs of 35, 49, 66 and 92 studied by Bridgeman et al have been used for this project. A calibration curve (HGI versus m) for the mill was plotted using the values for the coals. The HGI was then calculated as in Equation 3.9 (Bridgeman et al., 2010):

$$HGI_{equiv} = \frac{(m - \text{y intercept of the calibration curve})}{\text{Gradient of the calibration curve}} \qquad \text{(Equation 3.9)}$$

(a) (b)

Figure 3 7 (a) Stainless steel milling cup and milling balls and (b) Retsch PM100 ball mill

3.3.5.2: Particle Size Distribution.

To show the grindability of a biomass sample compared to coal in more detail, particle size distribution studies were performed. The sample was ground in the same way as in Section 3.3.5.2 using a ball mill. The sample was then sieved through a series of different size sieves; 600, 355, 212, 150, 75 and 53 μm and the mass of sample collected on each sieve was then measured and recorded as a percentage of the original sample mass. The average particle size of the sample collected on each sieve was calculated as the mid-point of two consecutive sieves and a cumulative graph of sample mass against average particle size was plotted. Along with the willow samples, particle size distribution curves were also plotted for the four reference coals mentioned in Section 3.3.5.1

3.3.6: Metal Analysis

3.3.6.1 Data from Rothamsted

The metal analyses for the SRC willow agronomy samples and the genetic samples sampled in December 2008 were all performed at Rothamstead Research using Inductively Coupled Plasma Spectrometry (ICP) with a nitric acid digestion using an Accuris ICPES (Inductively Coupled Plasma Emission Spectrometer). The plant material was dried for 4 hours at 80°C in an oven and cooled in a desiccator followed by acid digestion in which 0.250g of the oven-dried material was placed in a 25ml digestion tube, while 5ml of nitric acid was added around the side of the tube. The sample was then subjected to a whirl mix and placed at room temperature

for 2 hours, and then placed in heating blocks and left overnight. The final step involved the addition of 5ml of 25% of HCl and heating to 80°C prior to ICP analysis.

3.3.6.2 Data from Leeds

Metal analyses for the power station fuels were conducted at Leeds via ICP Spectrometry. 200mg of the sample was weighed followed by acid digestion in 69% acid with a dilution factor of 10:1. The digested sample was then analysed using a Perkin Elmer Optima 5000DV Inductively Coupled Plasma spectrometry.

3.3.6.3 Data from TES Bretby

The metal analyses for the second set of genetic samples which were sampled in February 2011 were provided by TES Bretby (TES Bretby Ltd, PO Box 100, BURTON-ON-TRENT, Staffordshire, DE15 0XD, UK) and were conducted by Inductively Coupled Plasma -Optical Emission Spectrometry (ICP-OES).

3.3.6.4: Silica Analysis

Silica analysis was conducted on samples ashed as in Section 3.3.1. 1.5g of sodium hydroxide was then melted in a nickel crucible and left to cool. 0.05g of ash was added to the sodium hydroxide melt and heated until dull red and the ash dissolved. It was then allowed to fuse for further 5 minutes before cooling it. 25ml of deionised water was added to the cooled mixture and the crucible was placed on a steam bath for 30 minutes. The contents of the crucible were then washed into a conical flask, and 20ml of 1:1 HCl was added to it and made up to a 1000 cm^3 solution. 10cm^3 of the solution was transferred to a 100cm^3 flask 1.5 cm^3 ammonium molybdate solution, 4 cm^3 tartaric acid, 1 cm^3 reducing solution were then added to the solution and it was diluted to 100cm^3 with deionised water. This was left to stand for an hour before measuring the absorbance at 650 nm using a Jenway 6000 Spectrophotometer, and comparing against standards prepared in a similar way.

3.3.7: Ash Fusion Tests

Ash fusion tests (AFT) were performed using a Carbolite digital ash fusion furnace shown in Figure 3.8, which has a black and white camera fixed at the front of the furnace to capture images of the ash whilst it is heated at a controlled temperature rate. The ash, which was prepared according to the British Standards mentioned in Section 3.3.1, was ground into a fine powder using an agate mortar. Test sample pieces were prepared by adding a few drops of demineralised water to the fine ash and making it into a paste and moulding it into small cylindrical pieces of 5 mm height x 5 mm diameter using a stainless steel mould. Addition of water could lead to the leaching of salts from the ash, hence water was added dropwise to minimize the leaching. The mould was lined with petroleum jelly to facilitate the easy removal of the test sample. The test samples were placed into the center of the furnace which was pre-heated to 550^{o}C one degree at a time to avoid thermal shock. These were then heated to 1500^{o}C at a heating rate of 10^{o}C/min in an oxidisng atmosphere with an air flow rate of 50 ml/min. Key stage temperatures, shrinkage starting temperature (SST), deformation temperature (DT), hemisphere temperature (HT) and flow temperature (FT) were determined according to British Standards (Solid biofuels, 2006)

Figure 3 8 Carbolite digital ash fusion furnace

3.3.8: Ash Melting Behaviour

The ash samples for which ash fusion tests were conducted were also analysed to explore their ash decomposition and melting behaviour using a Netzsch STA (Simultaneous Thermal analysis) 449C Jupiter®, coupled to a Netzsch QMS 403C

Aëolos Quadrupole Mass Spectrometer. Simultaneous thermal analysis involves the simultaneous application of thermogravimetry (TG) (which measures sample weight loss in a controlled temperature program) and differential thermal analysis (DTA) (which monitors the temperature difference between the sample and an inert reference material). 10mg of the ash sample was heated from 30 to 1400^{o}C at 10^{o}C/min in 12.5% O_2/He. The volatiles evolved were directly transferred into the electron impact ion source of the MS via a heated fused silica capillary. The gases/vapours and fragments detected were H_2O (m/z 18) C (m/z 12), CO (m/z 28), CO_2 (m/z 44), K (m/z 39), Cl (m/z 35), SO_2 (m/z 64) and KCl (m/z 74). Calibration of temperature and sensitivity was performed according to the standard melting points of five metals (Indium, Tin, Bismut, Zinc and Gold), and a buoyancy correction was also applied at the same heating conditions.

Figure 3 9 Netzsch STA (449C Jupiter®, coupled to a Netzsch QMS 403C Aëolos Quadrupole Mass Spectrometer.

3.3.9: Thermogravimetric Analysis (TGA)

Combustion and Pyrolysis studies were carried out via TGA as detailed in Sections 3.3.8.1 and 3.3.8.2

3.3.9.1: Pyrolysis studies

The pyrolysis tests for the power station fuels were carried out using a Netzsch STA 449C Jupiter simultaneous analyser. 10 mg of the sample (< 600 µm) was placed in a microbalance and heated to 900˚C at heating rates of 10˚C/min and

20°C/min under helium flowing at 50 ml min^{-1}. Mass loss curves and Differential Thermogravimetric (DTG) curves were obtained for each sample and were plotted against temperature. Apparent first order kinetics were calculated for the pyrolysis studies of the power station fuels using the constant reaction rate method detailed in Saddawi et al (Saddawi et al., 2009)

3.3.9.2: Combustion studies

Combustion tests for the agricultural residues and the SRC willow genetic samples were carried out using a Netzsch STA 449C Jupiter simultaneous analyser. 10 mg of the sample (< 600 µm) was placed in a microbalance and heated to 900°C at heating rates of 10°C/min and 20°C/min under 12.5% O_2/He flowing at 50 ml/min.

For the large agronomy data set, combustion tests were conducted using a Stanton Redcroft Simaltaneous analyser STA-780 series thermogravimetric analyser shown in Figure 3.9, to obtain mass loss curves and burning profiles. 5 mg of the sample was heated in a purge of air at a rate of 25°Cmin^{-1} to a final temperature of 900°C with an air flow of 50 ml/min. Mass loss curves were plotted from the data obtained and the DTG gave the burning profile from which the peak temperatures for the release of volatile matter and char combustion were obtained.

Figure 3 10 Stanton Redcroft Simaltaneous analyser STA-780 series

3.3.10: Pyrolysis Gas Chromatography-Mass Spectrometry (Py GC-MS)

Pyrolysis GC-MS was performed on the samples using a CDS 1000 pyroprobe coupled to a HP 5890 series II Gas Chromatograph fitted with a Rtx 1701 60 m

capillary column, 0.25 id and 0.25 µm film thickness. The oven was held at 70°C for 2 minutes and then programmed at 20°C min^{-1} to 250°C and held for 15 minutes. 1 mg of sample was placed in a 20 mm silica tube between two plugs of quartz wool and it was then pyrolysed at 250°C and 600°C with a nominal ramp rate of 20°C ms^{-1} and a final dwell time of 20 seconds. Products were identified via mass spectral detection (NIST05A MS library) and by comparison with data from the literature (Fahmi et al., 2007b, Nowakowski and Jones, 2008, Nowakowski et al., 2007).

3.3.11: Char preparation

High heating rate char were produced from the ground power station fuels using a CDS 1000 pyroprobe. 20-25 mg was placed in the silica tube between quartz wool plugs and pyrolysed under flowing argon at 1000°C with a nominal ramp rate of 10^4 K s^{-1} and a final residence time of 20 s. The actual heating rate is expected to be less than then this. E.g. 10^3 K s^{-1} has been measured by inserting a fine thermocouple into the tube (Azhakesan et al., 1991). Multiple runs were performed to obtain sufficient sample for analysis and to obtain a high heating rate char yield. The chars were analysed for their C, H and N contents as described in Section 3.3.2.

3.3.12: Thermogravimetric Analysis- Mass Spectrometry (TGA-MS) of chars

Temperature programmed combustion (TPC) experiments of the powerstation fuels chars were conducted in a Netzsch STA 449C Jupiter simultaneous analyser coupled to a Netzsch QMS-403C Aëolos quadrupole mass spectrometer for the analysis of the evolved gases. From the data produced and the char analysis, the conversions of char-N to nitrogen-containing species were estimated, and for DDGS the char-S to sulphur-containing species during combustion were estimated. Approximately 10 mg of char was heated in flowing 12.5% O_2/He, at a heating rate of 10°C/min to a final temperature of 600°C. In this instance up to 26 different species were monitored simultaneously and scanned approximately every 2.5 s throughout the experiment. The species monitored were m/z 14 (N_2^{2+} and CO^{2+}), 27 (HCN + tail end of m/z 28 signal), 28 ($^{12}C^{1}{}^{6}O$), 30 (NO + $^{12}C^{18}O$), 43 (HNCO and tail end of m/z 44 signal), 44 ($^{12}C^{16}O_2$ + N_2O), 46 (NO_2 + $^{12}C^{16}O^{18}O$), 52 (C_2N_2), m/z 64 (SO_2), m/z 60 (COS) and m/z 48 (SO^+). In order to correct for isotope contributions to m/z

30 and 46 and resolution limitations on m/z 27 and 43, a pure graphite (99.999 %, Aldrich-Sigma Co.), sample, was also analysed in the same way. Since this sample contains no nitrogen, the CO and CO_2 contributions to these four signals could be measured for our instrument and subtracted from the char measurement results. The graphite sample was heated under the conditions previously described but to a final temperature of 900°C. A calibration for detector response to the different species was not performed, and so the results can be used to compare evolution of the same species from different fuels, but not to compare absolute amounts of different species from the same fuel.

3.3.13: Single Particle Burning Experiments

The experimental setup is shown in Figure 3.11. Approximately 12 particles, each of 3 mm length, were selected for each of the 6 different genotypes of willow studied. These were then placed on scientific graphical paper and photographed to determine the shape and dimensions of each particle. Each particle was weighed and pierced with a needle which was placed in the top hole of the needle holder with the particle being vertical to the flame and the cooling sheath was placed over it. The meker burner was ignited and the cooling sheath was moved into the flame and then retracted so that the particle was exposed to the methane-air flame. Simultaneously, videos were captured for each particle using a Fuji HS10 Finepix high speed camera. The videos were then analysed using the software Avidemux 2.5 (32bits) which allows the examination of each frame captured on the video. The duration of volatile flame and char burnout were then determined for each video and plotted against particle mass.

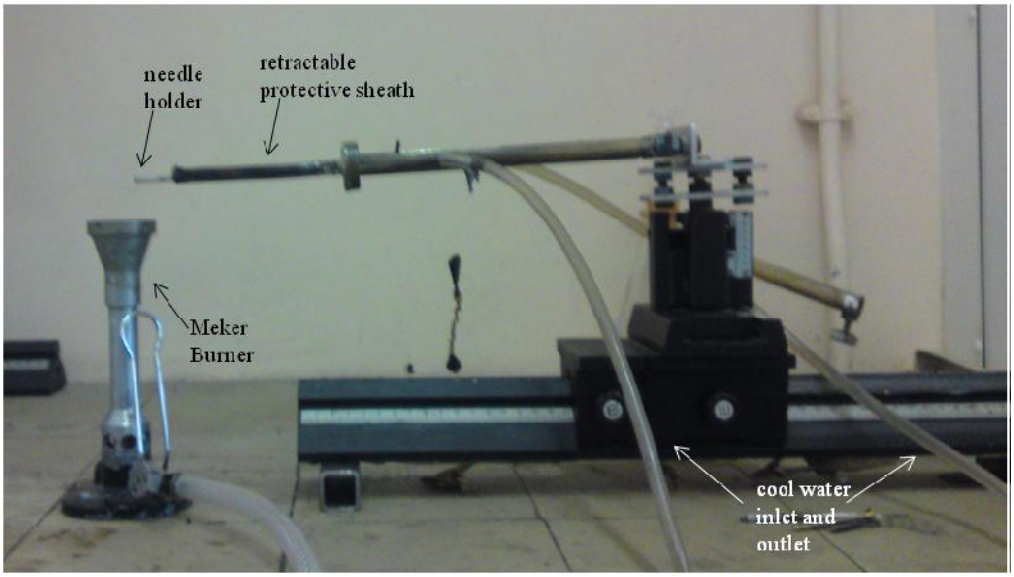


Figure 3 11 Water cooled sheath and needle set up along with meker burner.

Chapter 4

Fuel Characteristics and Thermal Properties of Some Imported Biomass Feeedstocks for UK Power Stations

4.1 Introduction

A very attractive process of utilising biomass for energy production is co-firing of biomass with coal as it can easily be retrofitted into existing power plants and it also helps to reduce the emissions of CO_2, SO_x and NO_x. In 2005 alone, 1.5 million tonnes of biomass was co-fired in the UK of which two thirds was imported (Perry and Rosillo-Calle, 2006). Agricultural wastes like, wood, palm residues and olive wastes were the major biomass feedstocks imported in the UK while shea residues are imported but in smaller quantities (Perry and Rosillo-Calle, 2006). Dried Distillers Grains and Solubles (DDGS) which was solely used as a feed for livestock due to its high protein and fibre content, has recently been shown a keen interest for being used as a feedstock in power stations (Giuntoli et al., 2009, Morey et al., 2009a). This is quite feasible since the production of bio-ethanol has increased remarkably from 17.25 billion litres in 2000 to 46 billion litres in 2007 and hence the co-products from this process need to be utilised (Balat and Balat, 2009). In this study 6 imported biomass samples (3 olive residues, Palm Kernel Expellers (PKE), shea residue and DDGS) were studied for their basic fuel characteristics, ash chemistry, thermal properties and their nitrogen chemistry. For the DDGS, further studies were done to determine the biochemical composition, investigate oil decomposition products at low temperatures and study the sulphur chemistry.

4.2 Materials and Experimental

4.2.1 Sample Preparation

The samples studied are detailed in Sections 3.2.1 to 3.2.4. All the samples were milled to particle sizes approximately 600 μm before any analysis was performed. The 3 olive residues will be referred to as Olive Residue A, B and C for this study as they are from different suppliers.

4.2.2 Experimental

All the experiments conducted are detailed in Section 3.3. Proximate, ultimate and metal analyses were done for the samples and their ash compositions were then calculated from the metal analyses. Pyrolysis studies were conducted both via Thermogravimetric Analysis (TGA) and Pyrolysis Gas Chromatography-Mass Spectrometry (py-GC-MS) to study the pyrolysis profile and detect the pyrolysis decomposition products respectively. From the pyrolysis profiles, apparent first order kinetics were also calculated. High heating rate chars were then prepared and analysed for their ultimates from which nitrogen partitioning of the fuel and char was calculated. The chars were then combusted in a Simultaneous Thermogravimetric Analyser coupled to a Mass Spectrometer (STA-MS) to study the conversion of char nitrogen to different nitrogen containing species. For the DDGS sample, py-GC-MS was also done at a low temperature of 250^{o}C. The sulphur partitioning and the conversion of char sulphur to sulphur containing species was also determined for DDGS.

4.3 Results and Discussion

4.3.1 Fuel Composition

The proximates, ultimates and calculated calorific values of the fuels are listed in Table 4.1. The biochemical composition has also been listed here. C and H contents of all the fuels are comparable while the N content of PKE and shea residue is almost two times greater than that of the olive residues and the N content of DDGS is approximately 2 to 4 times greater than that of the other residues. The sulphur contents of shea residue and DDGS are comparable but they are almost 3 times greater than that of olive residue B. The sulphur content of DDGS is relatively low compared to sulphur contents reported in previous studies of co-products of the dry-grind ethanol process which are 0.77 ± 0.18 wt% S. Olive residue C has the highest ash content while DDGS has the lowest ash content. The calculated calorific value of olive residue C is very low compared to the other residues due to the very high ash content, and as such lives outside of the validation range of the correlation equation.

Table 4 1 Ultimates, proximates and biochemical composition of residues.

Analysis	PKE	Shea	Olive Residue A	Olive Residue B	Olive Residue C	DDGS	References
C (% daf)	51.12	54.24	54.42	54.33	51.38	49.25	1. S. Carrióna, J.C. De Blasa,, J. Méndezb,
H (% daf)	7.37	6.58	6.82	7.2	6.32	7.27	A. Caídasa, P. García-Rebollara (2011) *Nutritive*
N (% daf)	2.80	3.48	1.4	1.39	1.45	5.88	*value of palm kernel meal in diets for growing*
S (%)[a](daf)	n.d.	0.3	n.d.	0.13	n.d.	0.39	rabbitsAnimal Feed Science and Technology165 79–84
O (%)[b](daf)	38.71	35.4	37.36	36.95	40.85	37.21	[2.]S. Pousga, H. Boly, J.E. Lindberg and B. Ogle (2007)
Cl (%) (daf)	n.a.	n.a.		0.284 [3]		0.17	*Evaluation of Traditional Sorghum (Sorghum bicolor)*
C/N	21.32	18.21	45.41	45.59	41.33	9.77	*Beer ,Residue Shea-Nut (Vitellaria paradoxa) Cake*
C/S	n.c.	482.13	n.c.	1114.46	n.c.	336.75	*(Gossypium Spp) Cake for Poultry in Burkina Faso:*
Moisture (% ar)	7.60	8.42	6.4	4.61	5.19	5.55	*Availability and Amino Acid Digestibility* International
Volatiles (% ar)	72.12	57.06	65.13	70.68	55.51	74.17	Journal of Poultry Science 6 (9): 666-672.
Fixed carbon (% ar)[b]	16.18	27.62	19.27	17.17	17.31	16.35	3. Teresa Miranda , Alberto Esteban , Sebastián Rojas ,
Ash (% ar)	4.10	6.9	9.2	7.54	21.99	3.93	Irene Montero and Antonio Ruiz (2008) *Combustion*
HHV (MJ/kg db)[c]	20.00	20.37	19.67	20.25	16.1	19.6	*Analysis of Different Olive Residues* International
Biochemical Composition (%)							Journal of Molecular Sciences9, 512-525
Hemicellulose	30.7 [1*]	25.9[2*]		14.4 [3]		21.66[*]	
Cellulose	22.08 [1*]	n.a.		12.4 [3]		7.63[*]	(Typical values from Literature)
Lignin	9.12 [1*]	n.a.		42.8 [3]		2.88[*]	
Total protein	16.2 [1]	6.7 [2]		n.a.		9.6	

[a] Data provided by RWE npower except for DDGS which was analysed at Leeds

[b] Calculated by difference. n.a. not analysed

[c] Data provided by Cranfield

[d] Calculated using Eqn 3.5

n.a. Data not available in literature

* Calculated using Eqns 3.6 and 3.7

n.c. not calculated

n.d. not determined

The main biochemical constituents in the fuels do not add up to 100% due to the presence of cell-wall bound water remaining even with oven drying along with some ash, some hydroxycinnamic acids (typically <1% DW), some proteins and the remains of other cell components The biochemical constituents in the DDGS sample, cellulose (7.63%), hemicelluloses (21.66%), lignin (2.88%), protein (9.6%), (cell bound water (5.55%) and ash (3.93%) add up to 53%. Hemicellulose is present in abundance compared to cellulose because it is easier to hydrolyse but harder to ferment compared to cellulose. The remaining 47% could presumably be the remains of non-digestible cell components.

4.3.2 Ash Composition and Slagging and Fouling Indices

The ash compositions of the fuels reported in Table 4.2 were calculated from the metal analyses measured by ICP spectrometry except for P_2O_5, SO_3 and SiO_2 which were measured directly and for some of the residues, these values were obtained from literature as the metal analysis of the fuel or the ash composition were not measured.. The total ash composition of some of the residues do not add up to 100 because the ash composition is reported only in the form of oxides. In reality, carbonates, hydrogen carbonates and sulphates are present (Baxter et al., 2012). It is also agreed by industry that it is common for biomass ash compositions to be <100% especially in cases where Ca is reported as an oxide and not as a carbonate (Seminar et al., 2009).

From Table 4.2, it can be seen that CaO, K_2O, MgO, P_2O_5 and SiO_2 are the major components present in the ashes of the residues. The presence of some of these constituents is quite problematic as they cause slagging and fouling in boilers decreasing their efficiency. The alkali index and the base to acid ratio are used to determine the fouling and slagging tendencies of a fuel respectively. The alkali index (AI) is expressed as the amount of alkali oxide in the fuel per unit energy of the fuel and is calculated as shown in Equation 4.1 (Jenkins et al., 1998).

$$AI = {kg\ (K_2O + Na_2O)}/{GJ} \qquad \text{Equation 4.1}$$

The alkali index has a lower threshold value of 0.17 kg alkali/GJ above which fouling can probably occur and an upper threshold value 0.34 kg alkali/GJ above which fouling certainly occurs (Jenkins et al., 1998).

The alkali indices reported for all the fuels in Table 4.2 are higher than the upper threshold value indicating that all the fuels certainly have a tendancy of causing fouling.

The base to acid ratio $R_{b/a}$ is expressed as a ratio of the basic components which include, CaO, MgO, K_2O, Na_2O and Fe_2O_3 to the acid components which include Al_2O_3, TiO_2, SiO_2 and P_2O_5 of the fuel and can be calculated as in Equation 4.2 (Lolja et al., 2002, Vincent R, 1987)

$$R_{b/a} = \left(\frac{(Fe_2O_3+CaO+MgO+K_2O+Na_2O)}{(TiO_2+Al_2O_3+SiO_2+P_2O_5)}\right) \qquad \text{(Equation 4.2)}$$

P_2O_5 gives a good correlation of $R_{b/a}$ with ash fusion temperatures (Baxter et al., 2012). For $R_{b/a}$ of coals (which does not include P_2O_5), a value < 0.5 indicates low risk of slagging while a value > 1 indicates high risk of slagging (IEA, 1994). These values are only valid for coal but further studies need to be done to understand the correlation between slagging indices and melting temperatures for biomass.

Table 4 2 Calculated ash composition from metal analysis and slagging and foulind indices

Ash composition (% db)	PKE	Shea	Olive Residue A	Olive Residue B	Olive Residue C	DDGS	References
Al_2O_3	0.87	1.29	1.94	0.85	2.74	0.29	[1.] S. Carrióna, J.C. De Blasa,, J. Méndezb, A. Caídasa, P. García-Rebollara (2011) *Nutritive value of palm kernel meal in diets for growing* rabbitsAnimal Feed Science and Technology165 79–84
CaO	11.9	5.51	15.44	9.4	19.49	7.24	
Fe_2O_3	5.7	2.37	2.14	0.75	5.29	0.32	
K_2O	21.43	42.57	31.04	32.08	4.41	33.54	
MgO	11.51	6.83	5.78	2.87	5.25	6.43	[2.] S. Pousga, H. Boly, J.E. Lindberg and B. Ogle (2007) *Evaluation of Traditional Sorghum (Sorghum bicolor) Beer ,Residue Shea-Nut (Vitellaria paradoxa) Cake (Gossypium Spp) Cake for Poultry in Burkina Faso: Availability and Amino Acid Digestibility* International Journal of Poultry Science 6 (9): 666-672.
Mn_3O_4	1.03	0.05	0.05	0.02	0.33	0.35	
Na_2O	0.41	0.95	0.47	0.33	0.35	5.92	
P_2O_5[a]	32.31 [1*]	8.2 [2*]		5.64 [3]		41.18	
SO_3[a]	n.a.	n.a.	n.a.	n.a.	n.a.	3.97	
SiO_2[a]	16.51	14.4	21.1	10.88	67.4	1.64	
Total ash compounds	101.67	82.17	83.6	62.82	110.9	100.88	[3.] Teresa Miranda , Alberto Esteban , Sebastián Rojas , Irene Montero and Antonio Ruiz (2008) *Combustion Analysis of Different Olive Residues* International Journal of Molecular Sciences9, 512-525
Slagging/Fouling indices							
Alkali index (kg Alkali/GJ)[b]	0.48	1.61	1.57	1.27	0.69	1.52	
Base to acid ratio[c^]	1.03	2.44	1.91	1.68	0.46	1.24	
Base percentage	50.94	58.23	54.87	45.44	34.79	53.45	

[a] Measured directly

[^] TiO_2 not included

[b] Calculated according to Equation 4.1

[c] Calculated according to Equation 4.2

[*] P contents in the fuel obtained from literature and then P_2O_5 calculated

[1], [2] and [3] obtained from literature as the metal analysis of the fuel or the ash composition were not measured

For the base percentages reported in Table 4.2, ash melting temperatures can be as low as or even lower than 1100°C according to the compiled results shown in Figure 4.1 previously published by Bryers (Bryers, 1996). The ash softening temperatures (hemisphere stage) stage of PKE, olive residue B and DDGS have been plotted on (Figure 4.1) to compare how the ashes of these residues behave compared to the ashes of coals and other types of biomass It is seen that olive residue B and PKE have comparable ash softening temperatures to high SiO_2 and K_2O biomass ashes, while DDGS ash melts at temperatures <815°C under reducing atmosphere. Under oxidising conditions, DDGS melts at a higher temperature of 890°C. Higher temperatures under oxidising atmosphere have also been reported for Miscanthus (Baxter et al., 2012).

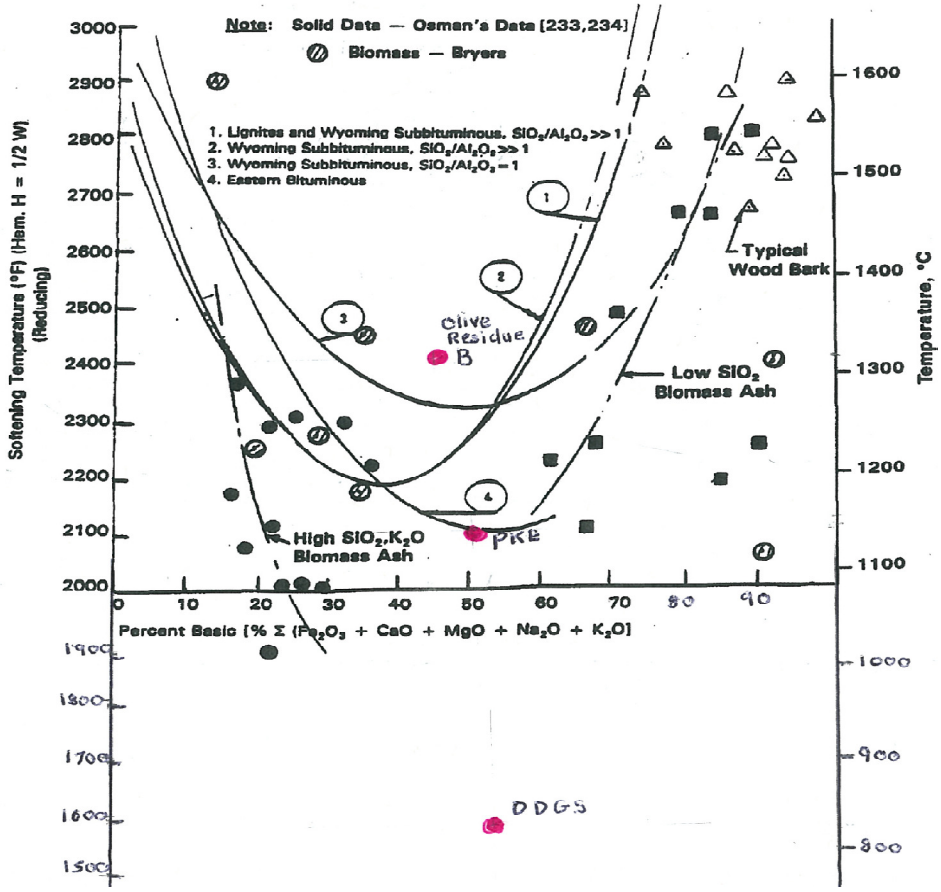


Figure 4 1 Hemisphere temperatures and base percentages of PKE, Olive Residue B and DDGS plotted with Bryers data. (Bryers, 1996)

4.3.3 Pyrolysis Studies

4.3.3.1 Thermogravimetric Analysis

The fuels were prolysed with a heating rate of 20°C/min (moderate heating rate) except for DDGS which had a heating rate of 10°C/min and their corresponding mass loss and time derivative of mass loss were plotted a (lower heating rate in order to be able to clearly separate the different processes occuring) shown in Figures 4.2 and 4.3 respectively. Two regions of mass loss are seen; an initial mass loss at temperature <120°C which is due to moisture evaporation and a larger mass loss due to the release of volatile matter. The residue that remains is the char. It is observed from Table 4.1 and Figure 4.2 that fuels with higher volatile matter content such as PKE and DDGS also have higher mass loss in pyrolysis while olive residue C which has the lowest volatile matter content also has the lowest mass loss in pyrolysis.

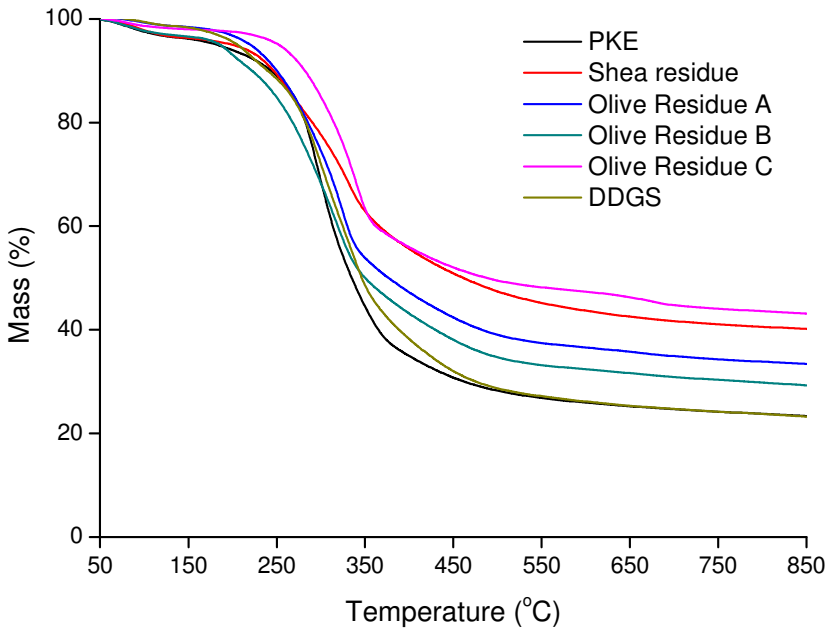


Figure 4 2 Mass loss curves against temperature for the fuels from TGA pyrolysis studies

The DTG curves shown in Figure 4.3 also show how the fuels behave under pyrolysis conditions. Olive Residue B and DDGS show a distinct peak between

190°C and 250°C which can be attributed to evaporation/decomposition of oils. In the case of DDGS, the most likely oils are glycerine, palmitic acid and linoleic acid which have boiling points of 290, 350 and 230°C respectively. These boiling points are higher than the peak temperatures reported in Table 4.3 but there could be some thermal degradation of the mixture occuring below these boiling points. This is discussed further in Section 4.3.2.2 where pyrolysis GC-MS was carried out at lower temperature (250°C) for the DDGS sample.

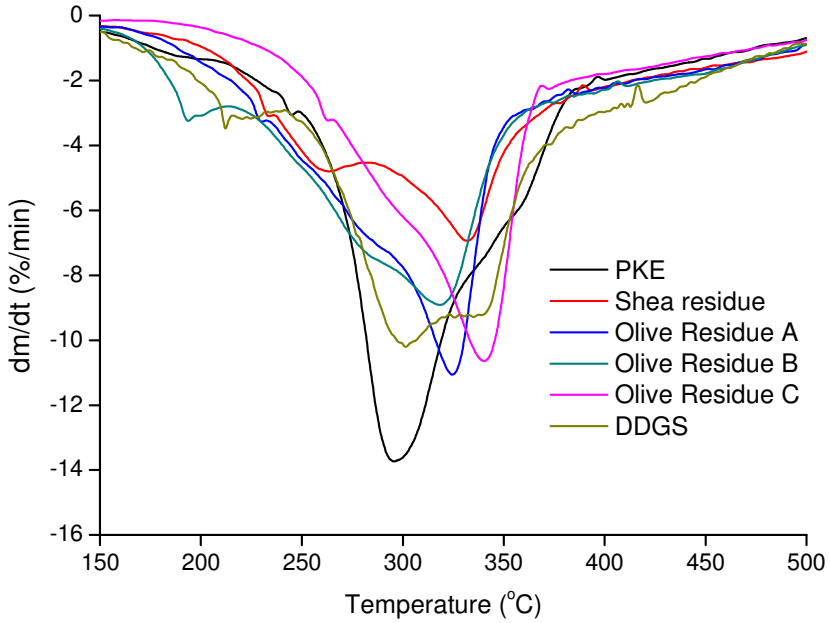


Figure 4 3 Derivative of mass loss (DTG) curves against temperature for the fuels from TGA pyrolysis studies.

At higher temperatures between 250 and 400°C large distinct peaks are observed. For PKE a single peak is observed while for shea resdiue, two partially unresolved peaks are seen. The three olive residues and DDGS show one distinct peak which is celluose decomposition with a shoulder at lower temperature which is attributed to hemicellulose decomposition. It has been reported in previous studies that hemicellulose decomposition occurs at lower temperatures (220-315°C) while cellulose decomposition occurs at higher temperatures (315-400°C) and lignin decomposes over a wide temperature range (Darvell et al., 2010, Giuntoli et al., 2009, Mansaray and Ghaly, 1998). For the DDGS sample, a more intense peak is

seen for the hemicellulose decomposition because more hemicellulose is present compared to cellulose as reported in Table 4.1. The temperature at which the rate of mass loss is the maximum is known as the peak temperature (T_{max}) which can be used to determine how reactive a fuel is. It is seen in Figure 4.3 that PKE has the lowest peak temperature making it the most reactive while olive residue C has the highest peak temperature making it the least reactive and this was confirmed by apparent first order kinetic calculations. The peak temperatures for all the fuels are reported in Table 4.3.

4.3.3.2 Apparent First Order Kinetics

Apparent first order kinetics were calculated from $k' = -\frac{1}{m_t - m_0} \times \frac{d_m}{d_t}$ which follows the Arrhenius function (Equation 4.3) where $\frac{d_m}{d_t}$ is the rate of mass loss (%/sec), m_t is the mass available for pyrolysis at any time, t and m_0 is a terminal mass which is the mass of the sample at the end of the pyrolysis process (usually taken at 600°C).

$$k = A\, e^{(-E/RT)} \qquad \text{(Equation 4.3)}$$

where, k is the reaction rate constant, A is the pre-exponential factor, E is the activation energy, R is the gas constant and T is the temperature. The kinetics for the fuels were calculated for a temperature range of 160-350°C except for olive residue B and DDGS for which kinetics were calculated for two different regions as illustrated in figure 4.4; region 1 where oil evaporation/decomposition occurred and region 2 where the biochemical components started decomposing. The kinetic parameters are reported in Table 4.3

From the results reported in Table 4.3, PKE and DDGS show fastest reactivity and shea and olive residue C the slowest when the rate of pyrolysis is calculated at 300°C for PKE, shea and olive residues A and C and region 2 of olive residue B and DDGS. For region 1 of olive residue B and DDGS, olive residue B shows faster reactivity than DDGS.

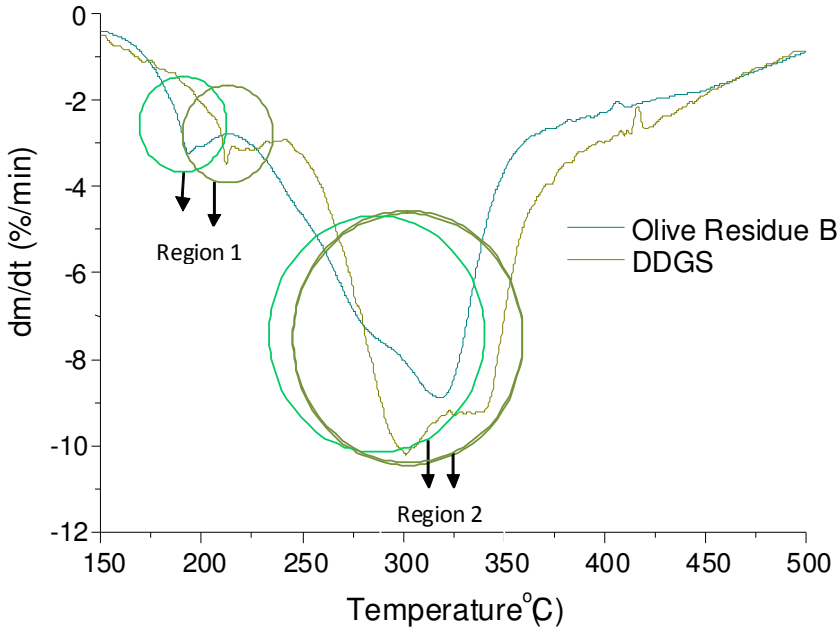


Figure 4 4 Derivative of mass loss (DTG) curves against temperature for the Olive Residue B and DDGS from TGA pyrolysis studies.

The activation energies reported in Table 4.3 are much lower compared to values found in the literature. The kinetic data for the thermal decomposition of PKE, shea and DDGS is very limited but an activation energy of 67 kJ/mol for shea has been reported by Munir et al (Munir et al., 2009). More data is available for olive wastes. For kinetics calculated for two stage decomposition of olive, cellulose and hemicellulose decomposition, activation energies of 87-162 kJ/mol and 215-287 kJ/mol respectively have been reported and for three stage decomposition of olive; hemicellulose, cellulose and lignin, activation energies of 91-109, 131-215 and 29-46 kJ/mol have been reported (Kastanaki et al., 2002, Skodras et al., 2006, Vamvuka et al., 2003). These low activation energies could be the result of the overlapping of oil/fat evaporation and decomposition of lignocellulosic components since all these residues are products from the oils and fat industries and the kinetic parameters represent global kinetics for the two processes. Linear regression curves illustrated in Figure 4.5 were plotted for all the residues and in the case of olive residue B and DDGS for the two different regions.

Table 4 3 Peak temperatures and kinetic parameters of the fuels from TGA pyrolysis studies

	T_{max} (^oC)	E ($kJmol^{-1}$)	ln A (s^{-1})	k_{300} (s^{-1}) $x10^2$	R^2
PKE	296	68	8.80	0.429	0.942
Shea	332	40	205.00	0.270	0.945
Olive Residue A	325	52	5.40	0.387	0.996
Olive Residue B					
Region 1	194	112	24.50	1.840	0.992
Region 2	318	45	4.00	0.409	0.997
Olive Residue C	340	71	9.00	0.289	0.997
DDGS					
Region 1	212	82	15.61	20.100	0.978
Region 2	302	75	10.25	0.411	0.995

k_{300} reaction rate constant at 300^{o}C for comparison between fuels

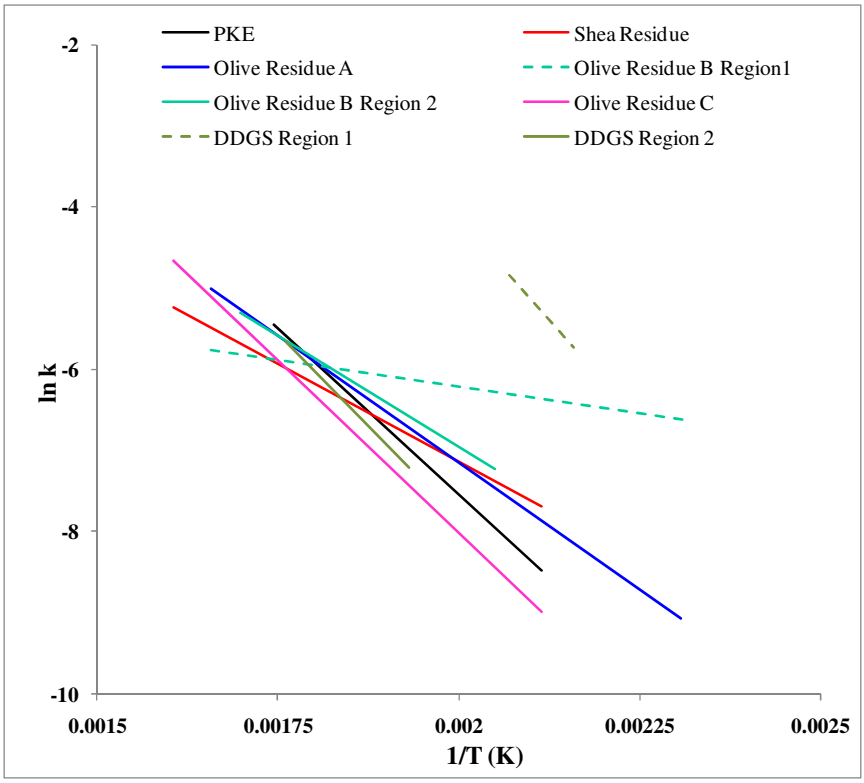


Figure 4 5 Linear Regression curves for all the residues

From Figure 4.5, it is seen that the two oily fuels (DDGS and olive residue B) have higher activation energies and faster reaction rates for Region 1 compared to Region 2. These values are comparable to those found in literature. The reaction rates of Region 2 are comparable to the reaction rates for the other 4 fuels but they have lower activation energies and slower reaction rates. This is because there may be the overlapping of oil evaporation and the decomposition of lignocelluloses components.

4.3.3.3 Pyrolysis Gas Chromatography-Mass Spectrometry (py-GC-MS)

The chromatograms for the PKE, shea residue, olive residue A, B and C and DDGS pyrolysed and 250^{o}C and 600^{o}C are shown in Figures 4.6-4.9 respectively. The corresponding peak identities of the components are listed in Tables 4.4-4.8 respectively. The peak identities have been determined from the NIST05A MS library and by comparison with previous work (Fahmi et al., 2007b, Nowakowski and Jones, 2008, Nowakowski et al., 2007). Most of the products detected are from

lignocelluloses and include methoxyphenols and furfural derivatives, and in the case of DDGS pyrolysed at 600^{o}C, some hetrocyclic aromatics like indole and pyrrole are also detected; these types of compounds are also detected during pyrolysis of amino acids (Darvell et al.). For DDGS pyrolysed at 250^{o}C (region 1 in figure 4.4), most of the products are long chain fatty acids and esters and furfural derivatives except for peak 4 which is an amino acid derivative. Py-GC-MS of the DDGS for Region 1 indicates the presence of furfural (boiling point of 162^{o}C and glycerine, and hence the weight loss in Region 1 (Figure 4.4) could be attributed to the evolution of these two (and other) species. Some of the peaks detected could not be realiably identified from the NIST05A library and they are suspected to be nitrogen containing compounds.

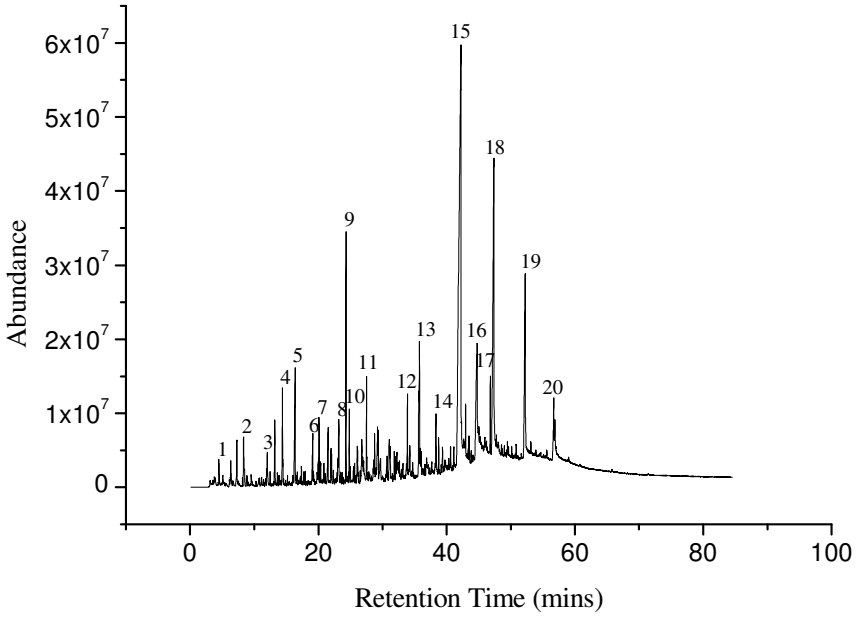


Figure 4 6 Py GC-MS chromatogram of PKE at T=600^{o}

Table 4 4 Peak identities of PKE

Peak	Compound	RMM	Marker
1	Furan, 2-methyl	82	-
2	Toluene	92	Lignin
3	Cyclopentene-3-(2-propenyl)	108	-
4	Furfural	96	Cellulose
5	2-Furanmethanol	98	Cellulose
6	1,2-Cyclopentanedione	98	Lignin
7	2-Furancarboxaldehyde, 5-methyl	110	-
8	1,2-Cyclopentanedione, 3-methyl-	112	Cellulose
9	Phenol	94	Lignin/Cellulose
10	Phenol, 2-methoxy-	124	Guaiacol lignin
11	Phenol, 4-methyl-	108	Hydroxyphenyl lignin
12	2-Methoxy-4-vinylphenol	150	Hydroxyphenyl lignin
13	Phenol 2,6-dimethoxy-	154	Syringol lignin
14	Phenol, 2-methoxy-4-(1-propenyl)-, (E)	164	Guaiacol lignin
15	Dodecanoic acid	200	Oil
16	D-Allose	180	Cellulose
17	Tetradecanoic acid	228	Oil
18	n-Hexadecanoic acid	256	Oil
19	Oleic acid	282	Oil
20	Octadecanoic acid	284	Oil

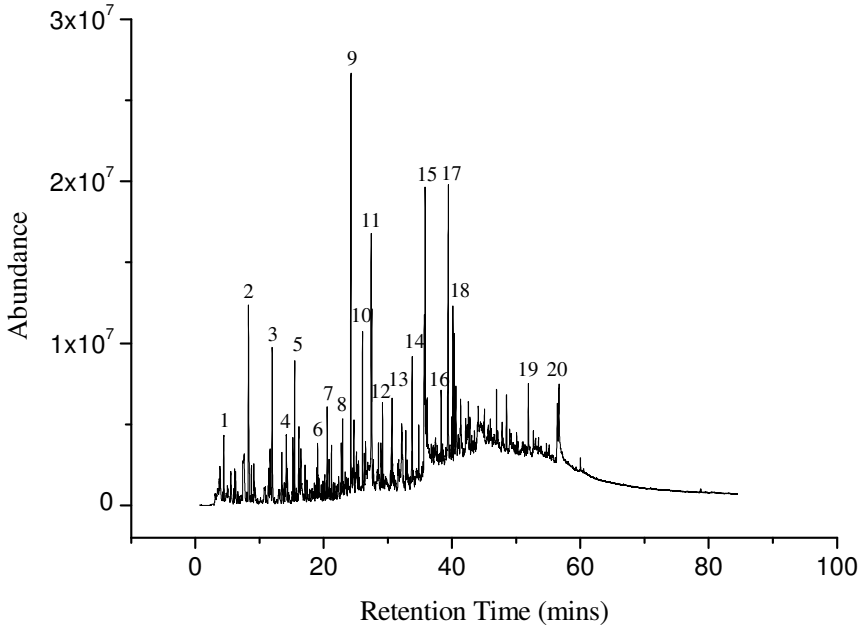


Figure 4 7 Py GC-MS chromatogram of Shea Residue at T=600^{o}C

Table 4 5 Peak identities of Shea Residue

Peak	Compound	RMM	Marker
1	Furan, 2-methyl	82	-
2	Toluene	92	LigninOil
3	Undetermined	-	-
4	Furfural	96	Cellulose
5	Undetermined	-	-
6	Undetermined	-	-
7	2-Cyclopentene-1-one, 3-methyl	96	Cellulose
8	1,2-Cyclopentanedione, 3-methyl-	112	Cellulose
9	Phenol	94	Lignin/Cellulose
10	Phenol, 2-methyl-	108	Hydroxyphenyl lignin
11	Phenol, 4-methyl-	108	Hydroxyphenyl lignin
12	Phenol, 2,4-dimethyl-	122	Oil
13	Phenol, 4-ethyl-	122	Hydroxyphenyl lignin
14	Benzene- 3 -butenyl	132	Oil
15	Undetermined	-	-
16	Undetermined	-	-
17	Undetermined	-	-
18	Undetermined	-	-
19	n-Hexadecanoic acid	256	Oil
20	Octadecanoic acid	284	Oil

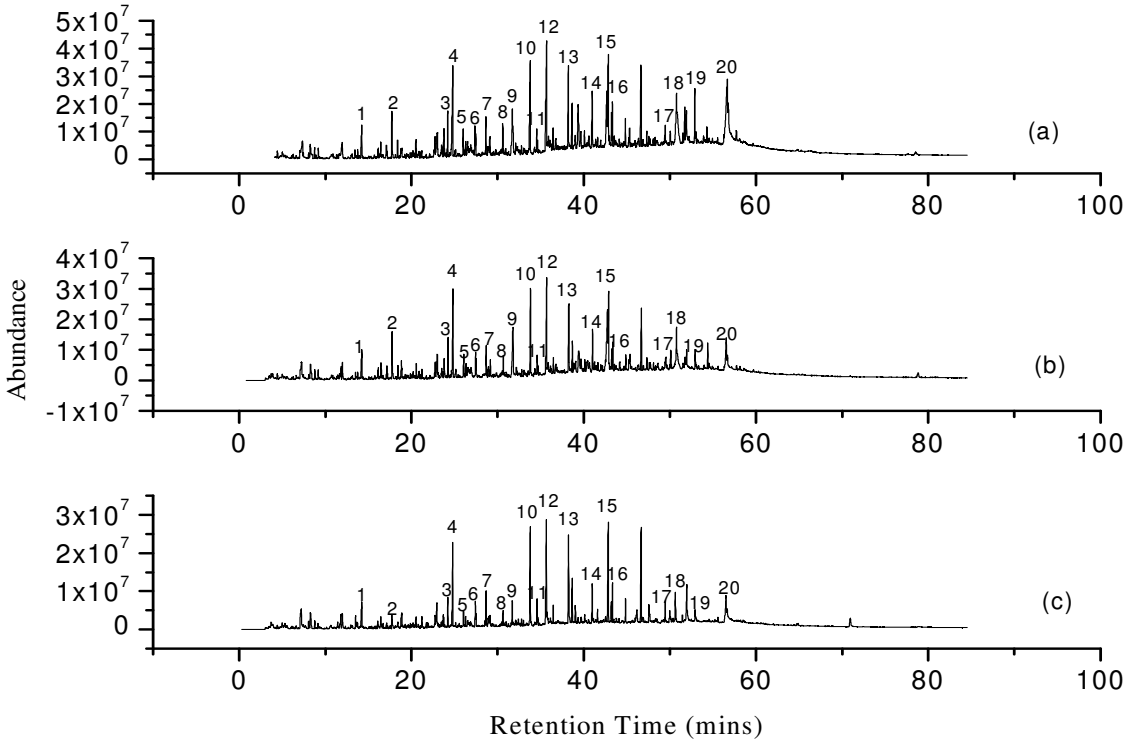


Figure 4 8 Py GC-MS chromatogram of: (a) Olive Residue A (b) Olive Residue B and (c) Olive Residue C at T=600^{o}C

Table 4 6 Peak identities of Olive Residues A, B and C

Peak	Compound	RMM	Marker
1	Furfural	96	Cellulose
2	Undetermined	-	-
3	Phenol	94	Lignin/Cellulose
4	Phenol, 2-methoxy-	124	Guaiacol lignin
5	Phenol, 2-methyl-	108	Hydroxyphenyl lignin
6	Phenol, 4-methyl-	108	Hydroxyphenyl lignin
7	Phenol, 2-methoxy-4-methyl-	138	Guaiacol lignin
8	Phenol, 4-ethyl-	122	Hydroxyphenyl lignin
9	Phenol, 4-ethyl-2-methoxy-	152	Guaiacol lignin
10	2-Methoxy-4-vinylphenol	150	Hydroxyphenyl lignin
11	Phenol, 2-methoxy-3-(2-propenyl)-	164	Guaiacol lignin
12	Phenol, 2,6-dimethoxy-	154	Syringol lignin
13	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)	164	Guaiacol lignin
14	Undetermined	-	-
15	Undetermined	-	-
16	Phenol, 2,6-dimthoxy-4-(2-propenyl)-	194	Syringol lignin
17	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)	196	Syringol lignin
18	Desaspidinol	-	-
19	9-Octadecanoic acid (Z)-, methyl ester	296	Oil
20	9-Octadecanoic acid, (E)-	282	Oil

Table 4 7 Peak identities of DDGS pyrolysed at 250^{o}C

Peak	Compound	RMM	Marker
1	Furfural	96	Cellulose
2	Glycerin	92	Oil
3	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	144	Amino Acid
4	Ethyl hydrogen succinate	146	-
5	2-Methoxy-4-vinylphenol	150	Guaiacol lignin
6	Palmitic Acid, ethyl ester	284	Oil
7	Palmitic Acid	256	Oil
8	Linoleic Acid	294	Oil

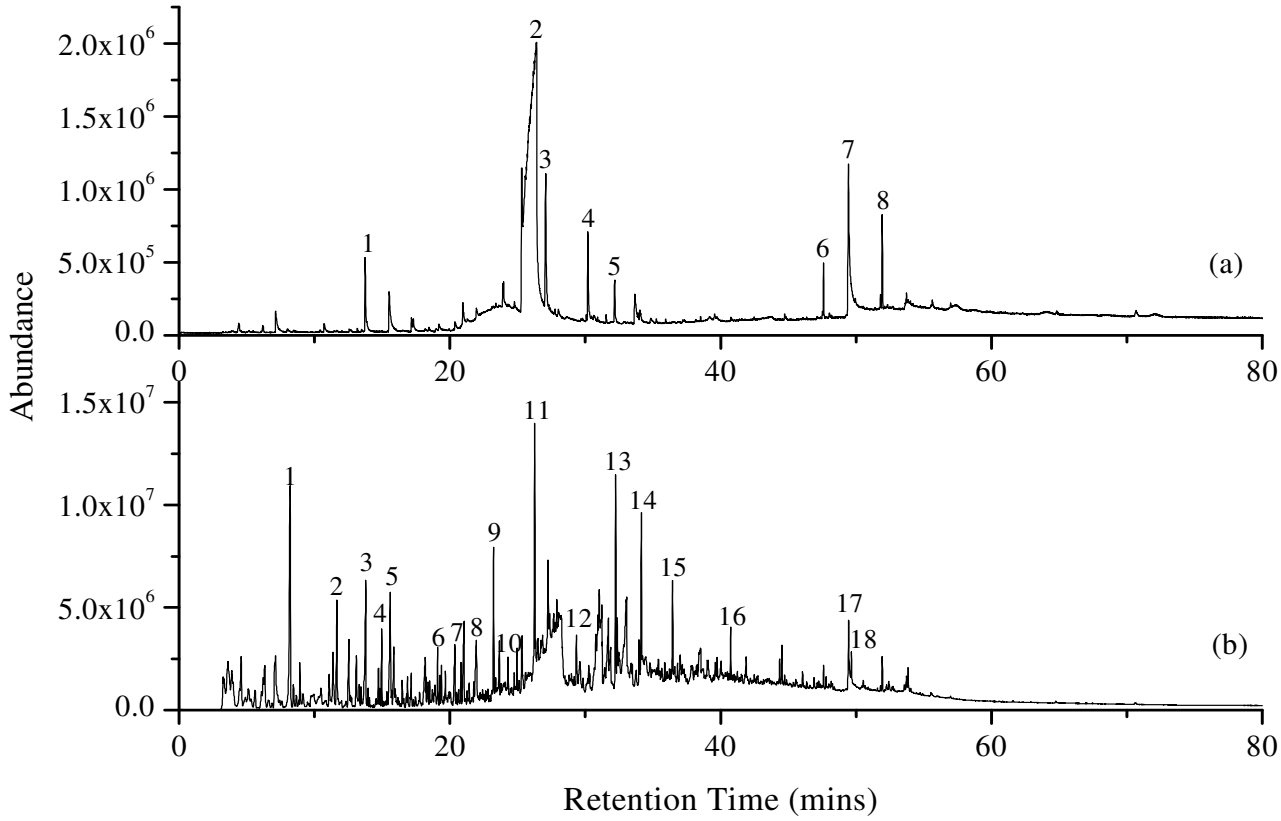


Figure 4 9 Py GC-MS chromatogram of DDGS pyrolysed at: (a) 250°C and (b) 600°C

Table 4 8 Peak identities of DDGS pyrolysed at 600^{o}C

Peak	Compound	RMM	Marker
1	Toluene	92	Lignin
2	Pyrrole	67	Amino Acid
3	Furfural	96	Cellulose
4	1H-Pyrrole, 3-methyl-	81	Cellulose
5	2-Furanmethanol	98	Cellulose
6	2-Furancarboxaldehyde, 5-methyl-	110	Cellulose
7	2(5H)-Furanone	84	Cellulose
8	1,2-Cyclopentanedione, 3-methyl-	112	Cellulose
9	Phenol	94	Cellulose
10	Maltol	126	Lignin/Cellulose
11	Phenol, 4-methyl-	108	Guaiacol lignin
12	Phenol, 4-ethyl-	122	Hydroxyphenyl lignin
13	2-Methoxy-4-vinylphenol	150	Guaiacol lignin
14	Indole	117	Hydroxyphenyl lignin/ Amino Acid
15	1H-Indole, 3-methyl-	131	Hydroxyphenyl lignin/ Amino Acid
16	4-Methyl-2,5-dimethoxybenzaldehyde	180	Syringol lignin
17	n-Hexadecanoic acid	256	Oil
18	Octadecanoic acid, 2-propenyl ester	324	Oil

4.3.4 Char Analyses

4.3.4.1 Char combustion kinetics

The mass loss and DTG plots for the high heating rate chars are presented in Figures 4.10 and 4.11 respectively. From the char yields reported in Table 4.10 it is seen that olive residue C, which has the highest ash content, also has the highest char yield, while PKE and DDGS which have lower ash contents have lower char yields. The chars of PKE and DDGS start combusting at higher temperatures compared to the other chars. It is illustrated in Figure 4.11 that PKE and olive residues A and C portray a single peak while shea residue, olive residue B and DDGS portray 2 overlapping peaks. The two stage char combustion could possibly be due to the presence of two different types of chars which could have resulted from the nature of different parts of the original fuels as has reported previously for shea (Munir et al., 2009) and olive (Kastanaki and Vamvuka, 2006).

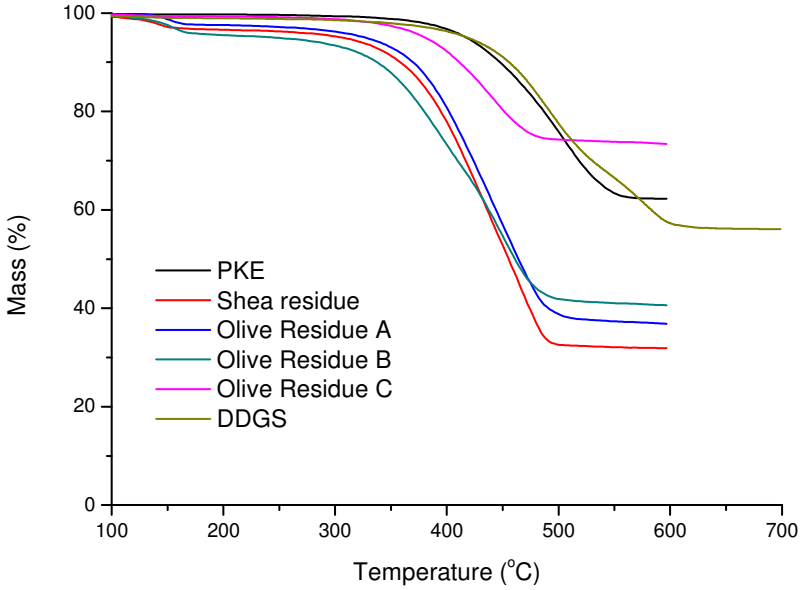


Figure 4 10 Mass loss curves against temperature for the chars from TGA char combustion studies

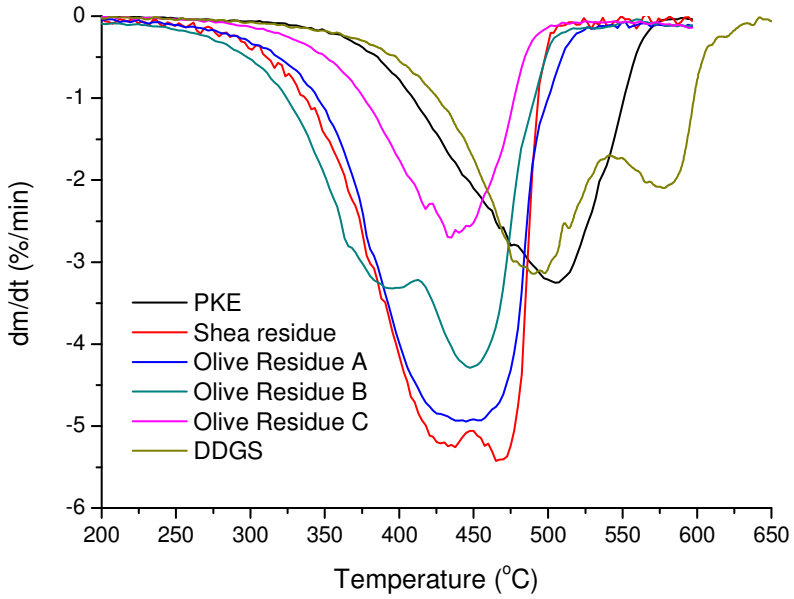


Figure 4 11 Derivative of mass loss (DTG) curves against temperature for the chars from TGA combustion studies.

Apparent first order kinetics were calculated as mentioned in Section 4.3.2.1.1 for the region between 300 -425°C for all the fuels except olive residue B and DDGS for which the kinetics were calculated for the two char combustion stages for the regions illustrated in Figure 4.12. Although shea residue also showed combustion occurring in two stages, kinetics could not be taken for the two stages because enough data points were not available and hence the kinetic parameters represent global kinetics.

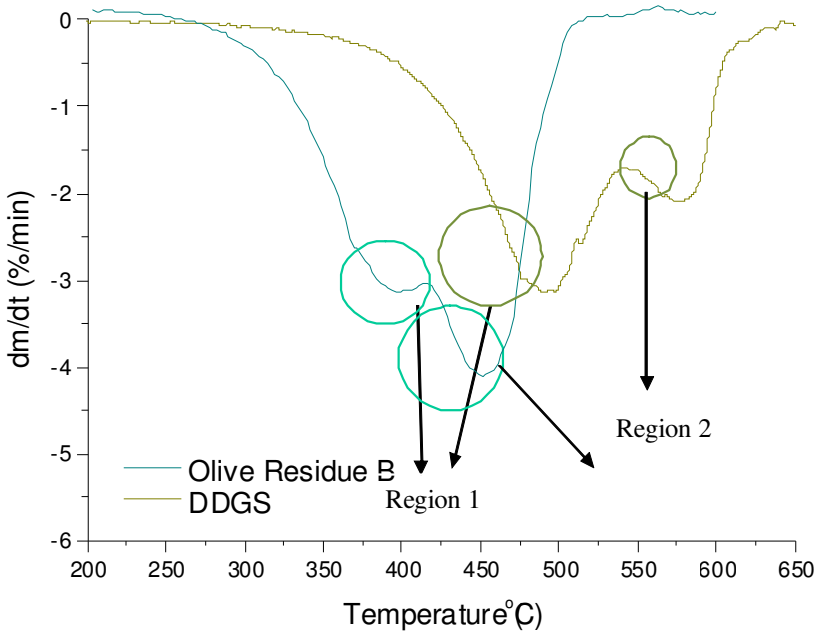


Figure 4 12 Derivative of mass loss (DTG) curves against temperature for the chars of Olive Residue B and DDGS from TGA combustion studies

The calculated kinetic parameters and the peak temperatures of the chars for both Regions 1 and 2 are reported in Table 4.8. From these values it can be interpreted that the DDGS char is the least reactive while olive residue B char is the most reactive and this is also illustrated on the DTG curves in figure 4.12 where DDGS has the highest peak temperatures while olive residue B has the lowest peak temperature. Activation energy values reported previously for olive char combustion are higher (approximately >140kJ/mol) compared to the values presented in Table 4.9. (Kastanaki and Vamvuka, 2006, Osvalda, 2007). Linear regression curves illustrated in Figure 4.13 were plotted for all the residues and in the case of olive residue B and DDGS for the two different regions.

Table 4 9 Peak temperatures and kinetic parameters of the chars from TGA combustion studies

	T_{max} (^oC)	Ea ($kJmol^{-1}$)	ln A (s^{-1})	k_{425} (s^{-1}) $x10^2$	R^2
PKE	505	102	10.50	0.084	0.993
Shea					
Region 1	438	91	9.80	0.279	0.818
Region 2	465				
Olive Residue A	445	94	10.40	0.303	0.992
Olive Residue B					
Region 1	395	132	19.30	3.187	0.988
Region 2	447	105	12.23	0.284	0.991
Olive Residue C	435	97	10.90	0.298	0.990
DDGS					
Region 1	490	128	14.74	0.066	0.997
Region 2	578	146	15.45	0.006	0.982

K_{400} reaction rate constant at 400^{o}C for comparison between fuels

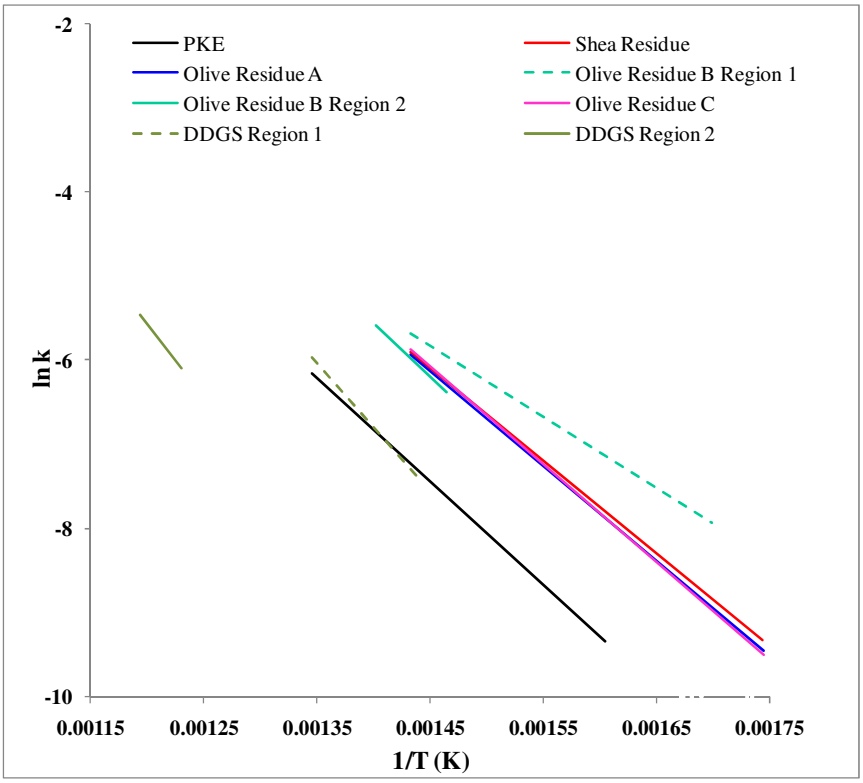


Figure 4 13 Linear Regression curves for all the residues

The kinetics for the DDGS and Olive Residue B were taken for 2 regions because the DTG curve illustrates that there maybe two types of chars present for these two fuels. From the reaction rates plotted in Figure 4.13, it is seen that the char in Region 1 of Olive residue B is the most reactive while that of DDGS for Region 2 is the least reactive. The chars of PKE and DDGS Region 1 are also less reactive compared to those of shea, olive residues A, C and B Region 2.

4.3.4.2 Fuel bound nitrogen and sulphur partitioning

Nitrogen partitioning was calculated for all the fuels and for DDGS, sulphur partitioning was also calculated by material balance using the C, H, N and S contents measured for the fuels and chars. The split of fuel nitrogen and sulphur between volatiles and chars during devolatilisation is known as partitioning. The proximates and ultimates of the chars and nitrogen and sulphur partitioning results are reported in Table 4.10. It is seen from the C/N and C/S ratios reported for the fuels and the chars in Tables 4.1 and 4.10 respectively that all the chars have lower

nitrogen contents compared to the fuels except for PKE which has comparable C/N ratios and DDGS has higher nitrogen content in the char compared to the fuel. This indicates that all the chars are depleted in nitrogen except DDGS which is enriched with nitrogen. The reason why DDGS and PKE chars have high nitrogen contents is due to the fact that the two fuels are very rich in protein. Low temperatures or short residence times favour the retention of nitrogen in char while high temperatures are more favourable for faster release of nitrogen compared to volatiles (Glarborg et al., 2003, Jan E, 1994). Furthermore, nitrogen is released more readily from biomass than coal (Glarborg et al., 2003, Jan E, 1994). The sulphur content in the DDGS char is lower than that in the fuel hence the char is depleted in sulphur. Previous studies have reported that approximately 35-50 % of total sulphur in wheat is evolved as volatiles at 400^{o}C but at higher temperatures of 950-1000^{o}C, the amount of sulphur given off as volatiles increases only slightly to 45-55% (Knudsen et al., 2004). Both the nitrogen partitioning and the types of products found depend on fuel type, temperature and residence time (Glarborg et al., 2003, Werther et al., 2000), and is reported to be almost comparable to the volatile content (Werther et al., 2000). For the nitrogen partitioning reported in Table 4.10, most of the nitrogen (79-91 %) is released with the volatiles and this is comparable to values reported for straw which are 80-88 % nitrogen being released with the volatiles in a temperature range of 600-1150^{o}C (Storm et al., 1999, Werther et al., 2000). For sulphur partitioning, approximately 94 % of the sulphur is given off with volatile

Table 4 10 Ultimate and proximate analyses of chars from the fuels and their corresponding nitrogen and sulphur partitioning

Analysis	PKE	Shea Residue	Olive Residue A	Olive Residue B	Olive Residue C	DDGS
C (% daf)	91.46	89.34	84.3	85.78	86.23	87.94
H (% daf)	2.74	3.14	2.5	2.64	3.48	2.29
N (% daf)	4.37	2.49	1.10	1.40	1.18	7.05
S (% daf)	n.a	n.a	n.a	n.a	n.a	0.79
O (% daf)[a]	1.43	5.04	12.1	10.17	9.12	1.93
C/N	24.41	41.92	89.48	71.40	85.57	14.55
C/S	n.c	n.c	n.c	n.c	n.c	298.18
Moisture (%)[b]	0.26	0.98	0.00	0.81	0.36	0.77
Ash (% db)[b]	62.44	32.20	36.78	40.9	73.65	57.71
Char yield (% db)[c]	14.76	39.59	26.95	33.06	44.38	18.48
Volatile yield (% db)[a]	85.24	60.41	73.05	66.94	55.62	81.52
N partitioning						
N (%) in volatiles	90.97	79.33	81.78	82.68	87.78	90.55
N (%) in char	9.03	20.67	18.22	17.32	12.22	9.45
S partitioning						
S (%) in volatiles	n.c	n.c	n.c	n.c	n.c	93.98
S (%) in char	n.c	n.c	n.c	n.c	n.c	16.02

a Calculsted by difference

b Data obtained from STA-MS combustion run (h.r. 10^{o}C/min)

c High heating rate chars prepared in pyrotube (h.r. 10^{o}C/ms)

n.a not analysed

n.c not calculated

4.3.4.3 Conversion of char nitrogen and sulphur during combustion

The conversions of the char nitrogen and char sulphur are shown in Figures 4.13 and 4.14 respectively. The species detected were m/z 14 (N_2^{2+} and CO^{2+}), 27 (HCN + tail end of m/z 28 signal), 28 ($^{12}C^{16}O$), 30 (NO + $^{12}C^{18}O$), 43 (HNCO and tail end of m/z 44 signal), 44 ($^{12}C^{16}O_2$ + N_2O), 46 (NO_2 + $^{12}C^{16}O^{18}O$), 52 (C_2N_2), m/z 64 (SO_2), m/z 60 (COS) and m/z 48 (SO^+). Biomass contains nitrogen mainly in the form of proteins. During devolatilisation, ammonia (NH_3) and HCN are the products formed although formation of NH_3 is more favourable then HCN in some cases.. At lower temperatures the most likely product to be formed is NH_3 while HCN, which is formed due to the cracking of cyclic amides, is most likely to be formed at higher temperatures. (Hansson et al., 2004, Ren et al., 2011). In this case NH_3 and N_2O could not be detected because of the lack of resolution between the species and the contribution of water m/z 17 in the former case, and CO_2 in the latter case. Figure 4.14 illustrates that signals m/z 30 (NO) and 14 (N_2^{2+}) are the most intense detected. HCN is a product for the PKE, olive residue B and DDGS char while C_2N_2 is only seen for the PKE and DDGS char. HCNO is only seen for the combustion of the DDGS char. Figure 4.15 illustrates that the signal at m/z 48 (SO) is slightly more intense than m/z 64 (SO_2). This could be due to the fragmentation of the SO_2 to SO. That is because the SO_2 could have presumably reacted with the carbon surface to form OCS or it could have reacted with the stainless steel components of the TGA. OCS could also be a product of the partial oxidation of organic sulphur (Jones et al., 1995)

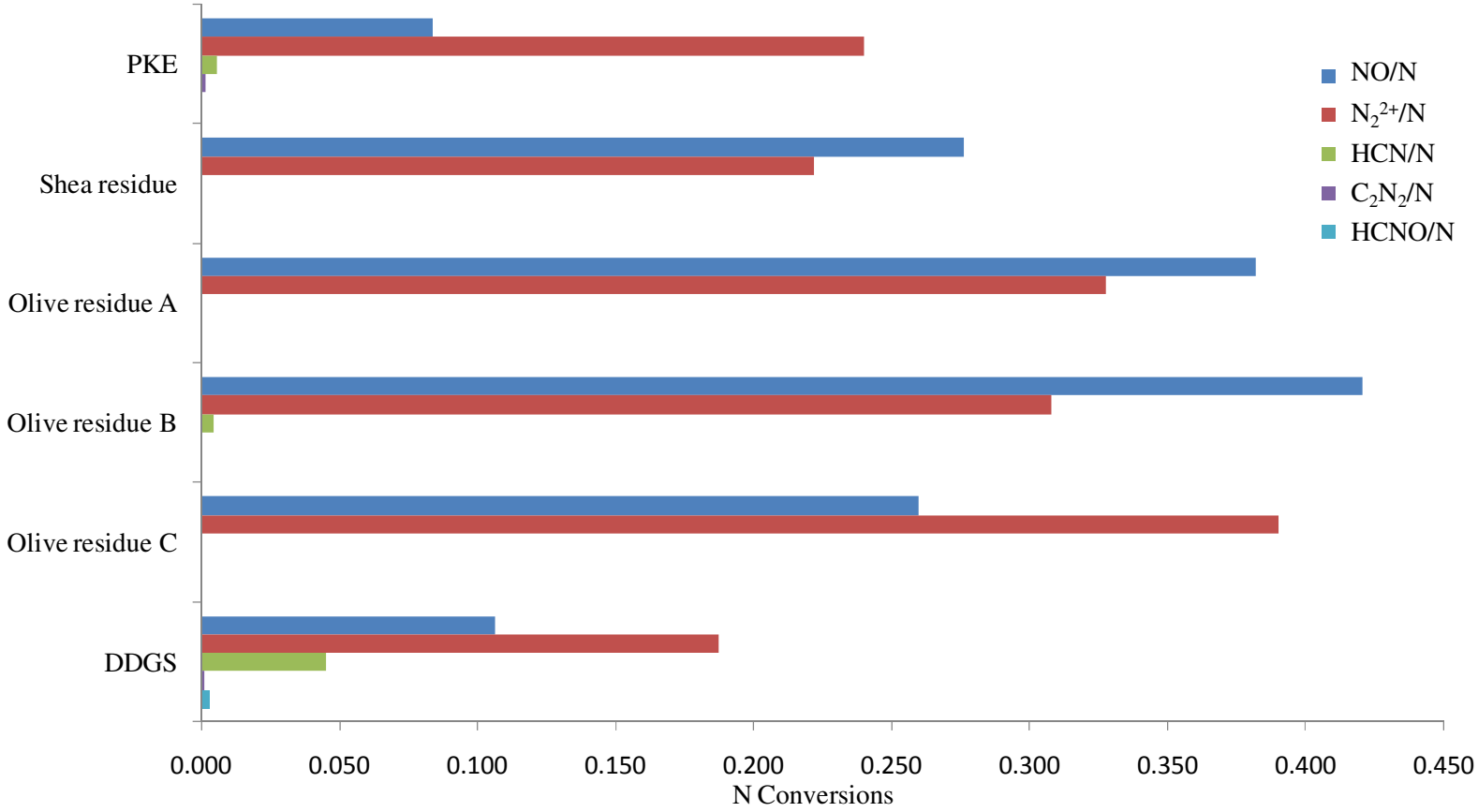


Figure 4 14 Char Nitrogen Species

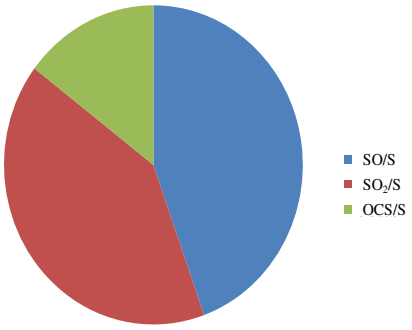


Figure 4 15 Sulphur Species for DDGS char

The nitrogen species evolution profiles of PKE, Shea residue and the three olive residues are illustrated in Figures.4.16, 4.17 and 4.18 respectively while the nitrogen and sulphur species evolution profiles for DDGS are illustrated in Figures 4.19a and b respectively.

In the case of PKE, olive residue A and C a single peak is seen for the CO and CO_2 species. All the nitrogen species are released at high temperatures except for HCN and C_2N_2 which are seen at slightly lower temperatures. The temperatures for the release of HCN and C_2N_2 are not very clear for olive residues A and C.

Shea and olive residue B show two peaks for CO_2 and CO indicating the presence of two types of chars. In both the cases, the char at higher temperatures favours the release of N species indicating that it is enriched with nitrogen. Just like in the other chars, the peak temperatures for the release of HCN and C_2N_2 are not very clear for these two chars either.

Two types of chars are also present for DDGS as shown by the two peaks for CO_2 and CO. In this case the S species were also detected. Interestingly enough it was seen that all the S species were released from the char at lower temperatures while most of the N species were released from the char at higher temperatures hence indicating that one type of char is rich in sulphur while the other is rich in nitrogen. In this case HCN and C_2N_2 seem to be overlapping between the two chars. HCNO is also released from DDGS char at high temperatures.

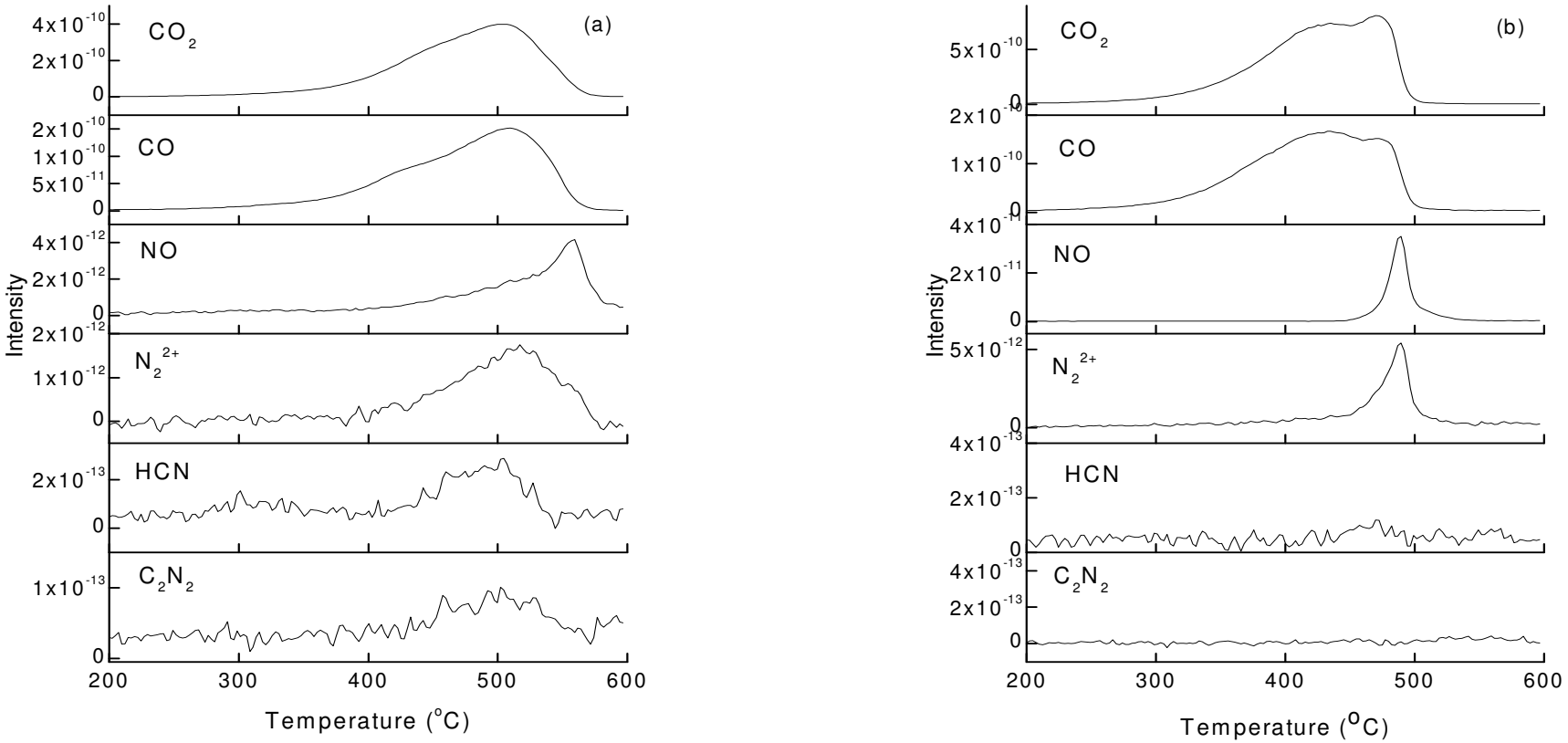


Figure 4 16 Evolution profiles of nitrogen species from char combustion for (a) PKE (b) Shea Residue

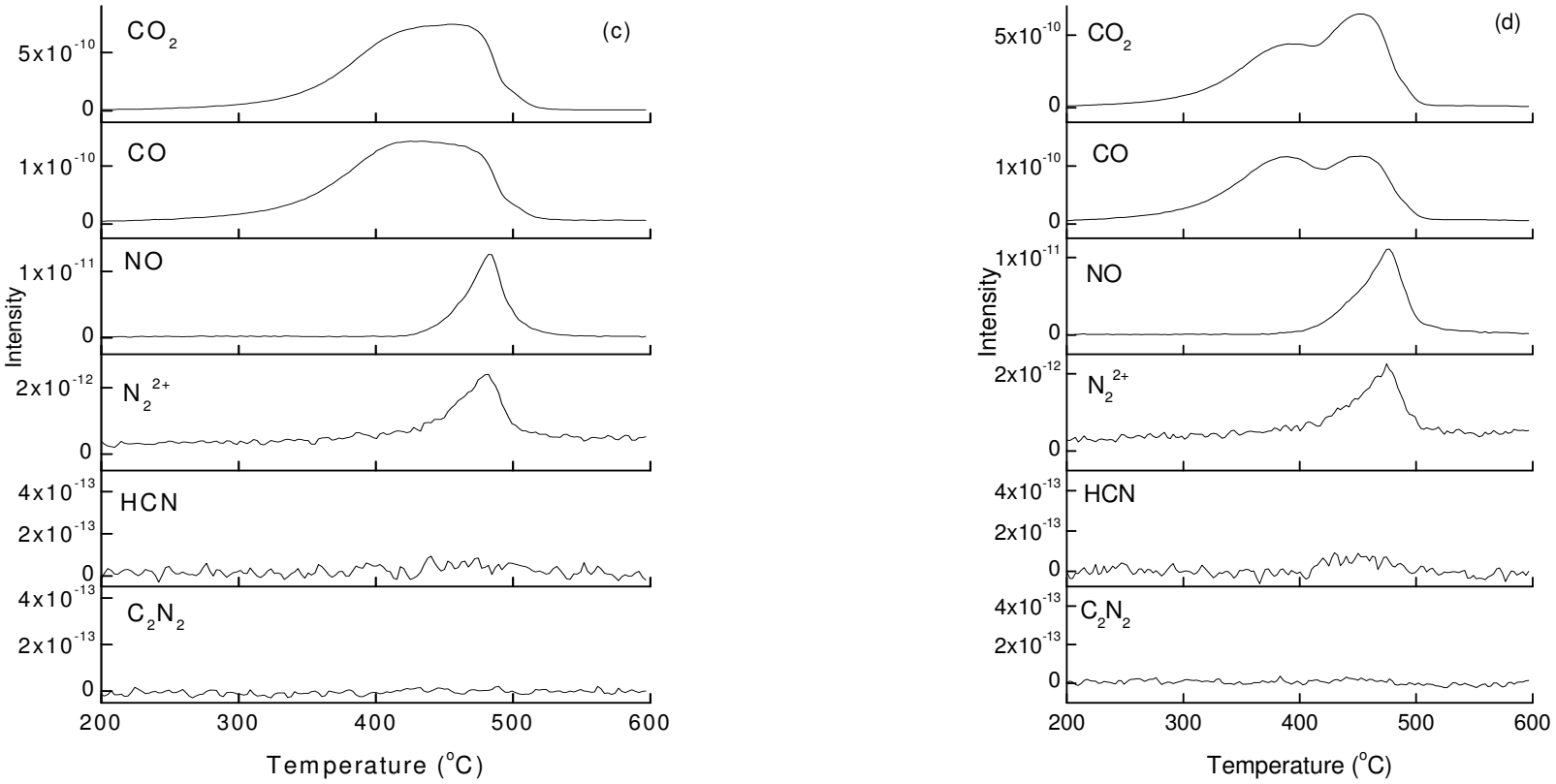


Figure 4 17 Evolution profiles of nitrogen species from char combustion for (c) Olive Residue A (d) Olive Residue B

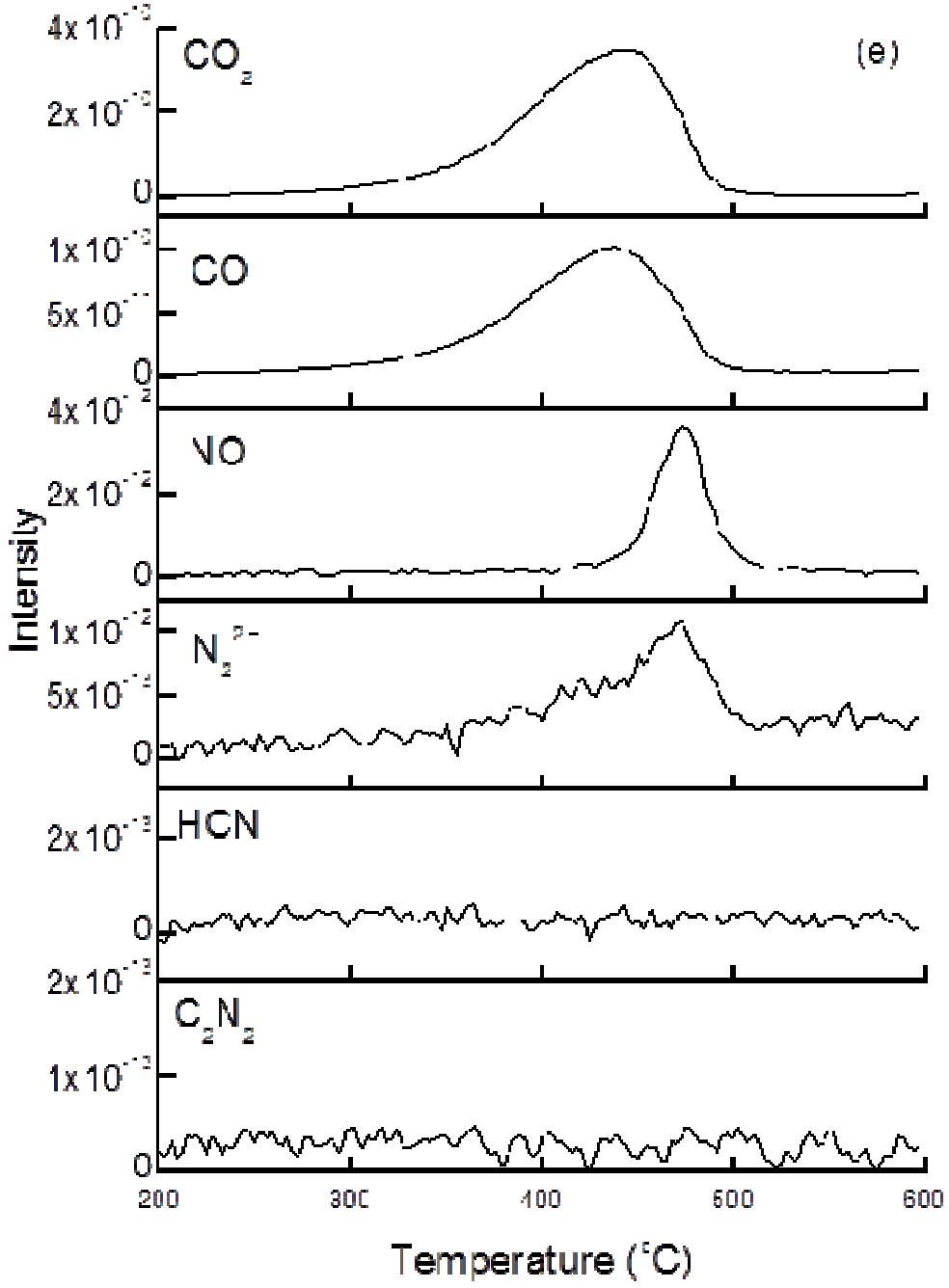
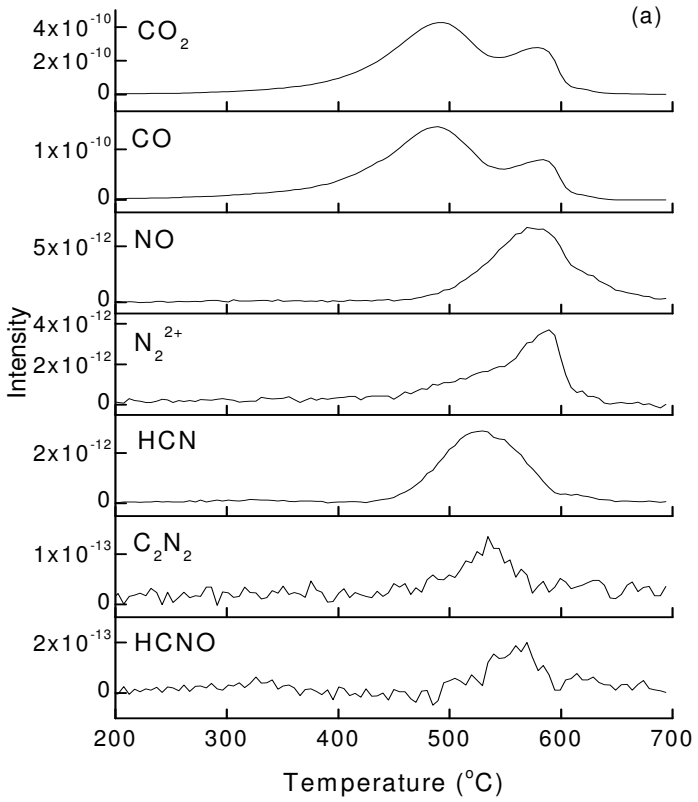


Figure 4 18 Evolution profiles of nitrogen species from char combustion for (e) Olive Residue C



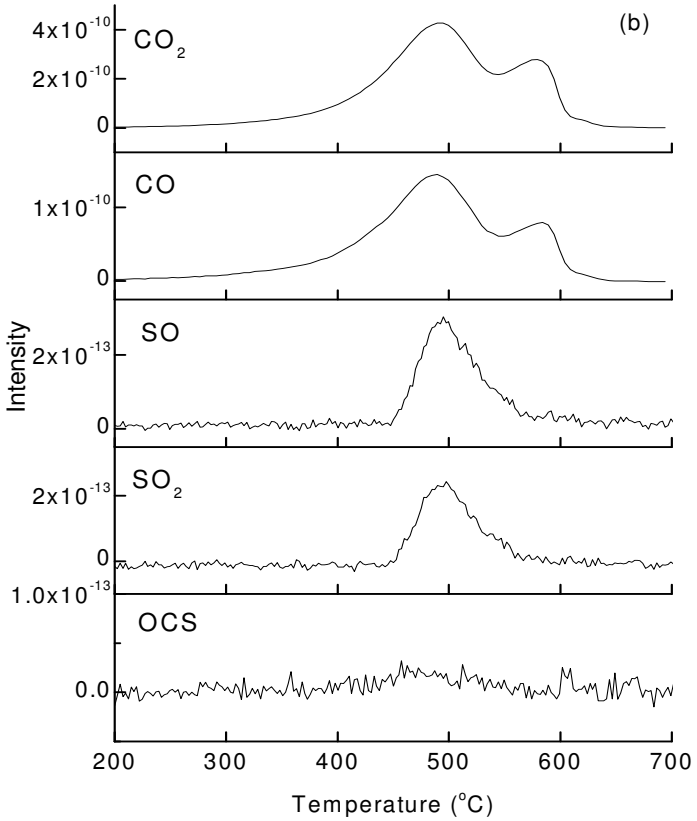


Figure 4 19 Evolution profiles for DDGS char combustion of (a) nitrogen species and (b) sulphur species

4.4 Conclusions

The carbon and hydrogen contents of all the fuels are comparable while the nitrogen content of PKE and shea residue are two times greater than thaose of the olive residue and the one for DDGS is almost 2-4 times greater than that of all the other residues. Shea residue and DDGS have fairly comparable sulphur contents which are 3 times greater than that of olive residue B. Olive residue C has the highest ash content and the lowest calorific value. All the fuels have a high tendency of fouling since they all have alkali indices > 0.34 kg/GJ. During pyrolysis, a small distinct peak is observed for the DDGS and olive residue B which is due to the evaporation/decomposition of oils. DDGS has a higher hemicelluloses content compared to cellulose because hemicelluloses is easier to hydrolyse but harder to ferment. DTGs from pyrolysis and first order kinetic parameters indicate that PKE is the most reactive fuel while olive residue C is the least reactive. For Py GC-MS done at 600^{o}C, most of the products detected were lignocelluloses and included methoxyphenols and furfural derivatives but in the case of DDGS, some hetrocyclic aromatics also detected in amino acid pyrolysis like indole and pyrrole were also detected. For samples pyrolysed at 250^{o}C the products mainly detected were furfural derivatives and big chain fatty acids and esters. During char combustion of PKE, shea residue and DDGS, two peaks were observed indicating that two different types of chars are present. Char kinetics indicate that the char of olive residue B is the most reactive while that of DDGS is the least reactive. From the nitrogen partitioning calculations 79-91 % of nitrogen is given off as volatiles and from sulphur partitioning of DDGS, approximately 94 % sulphur is given off as volatiles. From the C/N ratios of the fuels and chars it can be reported that all the chars except for DDGS are depleted in nitrogen and from the C/S ratios of the DDGS fuel and DDGS char, it can be reported that the char is depleted in sulphur. The major species detected from char combustion are NO and N_2^{2+} with small amounts of HCN in the case of PKE, olive residue B and DDGS. C_2N_2 was also detected from PKE and DDGS chars but HCNO was only detected from DDGS chars. SO and SO_2 were the major species detected in DDGS char. Most of the nitrogen species were detected at higher temperatures closer to the second peak of char combustion except for HCN and C_2N_2 which were detected at slightly lower temperatures. All the sulphur compounds for the DDGS char were detected at lower temperatures closer to the

first peak of char combustion. Hence it can be concluded that one type of char from DDGS is rich in sulphur while the other is rich in nitrogen.

Chapter 5

Fuel Properties of SRC Willow under different agronomic treatments

5.1 Introduction

The number of dedicated biomass plants and the existing coal plants which have resorted to co-firing has increased in the UK over the past few years. This is because energy production from biomass is not intermittent. The main concern with biomass is its availability and sustainability. There is a huge global potential of producing sufficient biomass with proper exploitation of resources, and a possibility of 10% of the global market available in the UK (Huhne et al., 2011). The UK Government wants to ensure biomass sustainability and hence from April 2013 Renewable Obligations (RO) support will only be given to liquid biofuels which reduce greenhouse gas emissions by 35% and for solid and gaseous biomass which will reduce carbon dioxide emissions by 60% and these biomass cannot be sourced from land that is vital for carbon accumulation and biodiversity (Huhne et al., 2011).

Some dedicated energy crops like Short Rotation Coppice (SRC) Willow and Miscanthus are of great interest for producing cleaner (low CO_2 emissions compared to fossil fuels) and renewable energy in UK power stations, since they are fast growing and sustainable. These crops require the macronutrients nitrogen, potassium and sulphur for growth. SRC willow has potential to remediate sewage sludge which also contains nutrients crucial to the growth of the willow, and therefore has sometimes been used in place of a conventional fertilizer. It is of interest to examine the combustion characteristics of willow produced under different growing regimes which might be received from a farmer by an energy or heat supplier.

The work reported here is a large study undertaken as part of the UK Supergen Bioenergy Consortium (www.supergen.bioenergy.net) activity, where willow was grown by Rothamsted Research Harpenden under a range of fertilizer regimes. Samples for each treatment were taken from triplicate plots twice a year (in autumn and spring) for a three year cycle and these samples were studied for their fuel and thermochemical conversion properties.

In this study the fuels were characterised for their basic fuel properties along with the ash composition and predicted slagging and fouling tendencies. In addition

to this, combustion studies were performed via Thermogravimetric Analysis (TGA). The characteristic combustion temperatures are reported from the burning profiles, and the catalytic impact of some metals on the volatile and char combustion is discussed Due to the dataset being so large, statistical analyses have been carried out to interpret better the differences between treatments and different sampling times.

The samples were analysed for their chlorine (Cl) contents but Cl was present in minute quantities (<0.02%) hence has not been reported in this work. Trace metals are not investigated here since their measurements had large errors on them given that they were present in small quantities, hence difficult to detect accurately. SiO_2 was also measured but only for a sub-set of the samples. The rest of the metals have all been measured and reported here.

5.2 Materials and Experimental

5.2.1 Materials

The fuels analysed in this study are described in detail in Section 3.2.5.2. The 6 fertiliser treatments that were applied are again listed in Table 5.1 for the purpose of this chapter. The samples taken in autumn each year are split into leaves and stems while the ones taken in spring are just the stems as there were hardly any leaves in spring. At each sampling time, samples from each triplicate plot for all 6 treatments were taken. Thus, in autumn six samples were taken from each treatment (three leaves and three stems) while in spring only three samples were taken from each treatment (three stems).

Table 5 1 Fertilizer Treatments applied to SRC Willow

Treatment	Fertiliser application per hectare (single plot area 6 x 10.5 m)
A	0 Kg N as $NH_4(NO_3)$
D	150 Kg N as $NH_4(NO_3)$
F	250 Kg N as $NH_4(NO_3)$
J	100 Kg K as K_2O + 150 Kg N $NH_4(NO_3)$
N	80 Kg SO_3 as $(NH_4)_2SO_4$ balanced to give 150 Kg N as $NH_4(NO_3)$
O	Sewage pellets

5.2.2 Experimental

The proximate, ultimate and metal analyses were carried out as detailed in Section 3.3. Metal analyses were carried out at Rothamsted Research and the corresponding ash compositions and fouling and slagging indices were calculated according to Equations 4.1 and 4.2 respectively. The silica analysis was only carried out for a sub-set of samples hence the base to acid ratio (slagging index) was only calculated for those samples (Jenkins et al., 1998, Lolja et al., 2002, Vincent R, 1987). The calorific values were calculated according to Equation 3.5 (Friedl et al., 2005) using the results from the ultimate analysis. Combustion studies were carried out via TGA with an air flow of 50ml/min and a heating rate of 25^{o}C/min from 40^{o}C to 900^{o}C. Statistical analyses were done using a package called Genstat (Genstat* 2011 Thirteenth Edition, VSN International). The training courses for Genstat at Rothamsted Research are based on (Payne, 2009).

5.3 Basic Statistical Concepts

5.3.1 Experimental Design

A good experimental design is one in which treatment differences can be estimated with minimum experimental bias and good experimental precision. The former can be achieved by randomisation and the latter is improved by replication and blocking. For the SRC willow fertiliser trial experiment all 3 concepts have been applied and these are explained in more detail here.

5.3.1.1 Randomisation

The random allocation of treatments to experimental units is used to fairly assess treatments without being bias and provides insurance against any unknown difference between experimental units.

5.3.1.2 Replication

Replication is the application of a treatment to more than one experimental units and the number of replicates is the number of times each treatment is applied. It is important to have replicates as it improves the experimental precision by giving extra information on the treatment effect. Additionally information on the background variation (noise) from variation between replicates of each treatment can be obtained and this is a good estimate against which treatment differences can be judged. Treatments usually have equal replicates but treatments of great interest can have more replicates.

5.3.1.3 Blocking

The grouping of homogenous experimental units together is known as blocking and is used to control variation. With blocking, background variation is split into two groups; variation due to blocks and variation due to residuals (variation in replicates). Hence the precision of the estimate of treatment differences increases. Blocking will often reflect the physical structure of the experimental units. For example, the drainage across a field may be different hence blocks having similar drainage conditions and at least one replicate of each treatment can be created.

For the SRC willow fertiliser trial, 15 treatments were applied with 3 replicates for each treatment and the experiment was divided into 3 blocks with one replicate for each treatment in each block. A schematic diagram showing the experimental design is in Appendix A.

5.3.2 Statistical Inferences

A statistical inference is an estimate of the properties of a population derived from the analysis of a sample obtained from it. Statistical inferences are of two types; point estimation, and hypothesis testing.

5.3.2.1 Point Estimation

Point estimation is the process of estimating using mathematical formulae, one or more summary statistics from the sample data that will represent our "best guesses" of the population parameters. *Mean* and *Variance* are the two commonly estimated and used statistics where the mean is the center point of the data distribution and the variance is the measure of spread that quantifies the amount of variation in the sample. The square root of the variance is the *Standard Deviation*.

5.3.2.2 Hypothesis Testing

Hypothesis testing is a form of inference where a given hypothesis for a population is tested based on a random sample (For example, a decision needs to be made on whether the nitrogen contents of SRC willow for different treatments are different or not based on measurements made in the laboratory).

In this process two hypothesis are defined; the null hypothesis, H_0 which represents no difference between treatments and the alternative hypothesis, H_1 which represents at least one difference between treatments. To test a hypothesis, a test statistic is required which has a known statistical distribution if the null hypothesis is true. Two most commonly used test statistics are the *t-test* and the *F-test*.

- **Degrees of Freedom (df):** The number of independent pieces of information on which a test is based is known as its degrees of freedom. dF needs to be specified for both the t-test and F-test. It can be calculated as the number of contributions minus the number of implicit constraints imposed. For example, for a comparison between 6 treatments, df = 6 – 1 =5 as one df has to be subtracted for the overall mean.

Table 5 2 Degrees of freedom for leaves and stems for the N, K, S and Sewage Pellets effects

		df leaves	df stems
N effect	Treatment	2	2
	Time	2	5
	Treatment.Time	4	10
K effect	Treatment	2	2
	Time	2	5
	Treatment.Time	4	10
S effect	Treatment	2	2
	Time	2	5
	Treatment.Time	4	10
Sewage pellets effect	Treatment	5	5
	Time	2	5
	Treatment.Time	10	25

Where: Treatment = df for different treatments

Time = df for different sampling times

Treatment.Time = df for interaction between treatments and sampling times

- **T-test:** The t-test compares the difference between sample means for each group taking the background variation into consideration. A larger deviation between sample means compared to the background variation indicates that there is a difference between two population means. A t-statistic can be calculated as in Equation 5.1

$$t_0 = \frac{\left(\bar{y}_1 - \bar{y}_2\right)}{\sqrt{s_p^2 \times \left(\frac{1}{n_1} + \frac{1}{n_2}\right)}} \qquad \text{Equation 5.1}$$

where $\bar{\mathbf{y}}_1$ and $\bar{\mathbf{y}}_2$ are the sample means for groups 1 and 2 respectively, s_p^2 is the pooled estimate of variance for the two treatments and n_1 and n_2 are the observations made for groups 1 and 2 respectively. The t distribution is a bell shaped curve with limits from - infinity to + infinity as shown in Figure 5.1. A critical value of significance level α corresponds to a value in the distribution such that there is a probability α of the observed statistic taking a value that size or bigger. If t_0 lies in the regions $-t_0 < -t_\alpha$ or $t_0 > t_\alpha$, then there is a significant difference between the two treatments. The value chosen mostly for the level of significance α is usually 0.05. (but can also be 0.10, 0.01 and 0.001).

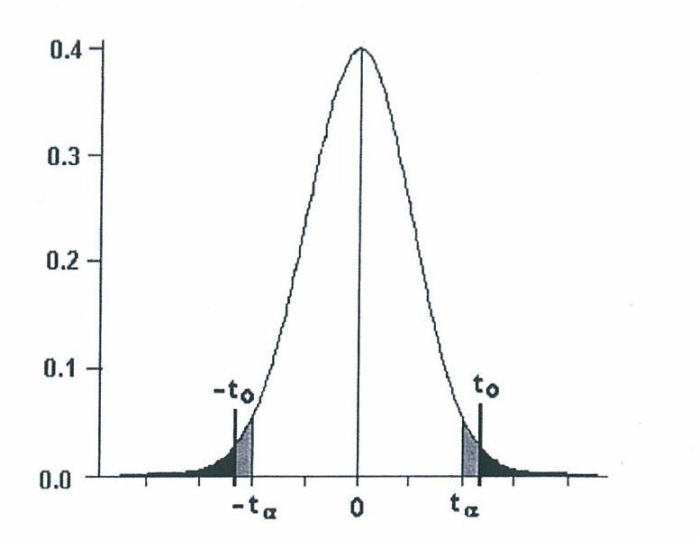


Figure 5 1 Two sided student's t-test with a significance level α

- **F-Test:** The F-test is an extension of the t-test and is used to compare the means of more than two treatments. The overall variability in the data set is split into "difference due to treatments" and "background/residual variability". The ratio of treatment variability/residual variability gives the variance ratio (F value) and the F values can be compared with tabulated values (p values) to check for evidence against the null hypothesis. There are two associated df for the F-test, one for the numerator and the other for the denominator. A significance level of 0.05 is used for the F-test for SRC willow. If $p < 0.05$ then at least one treatment difference exists. Figure 5.2 shows the F-distribution.

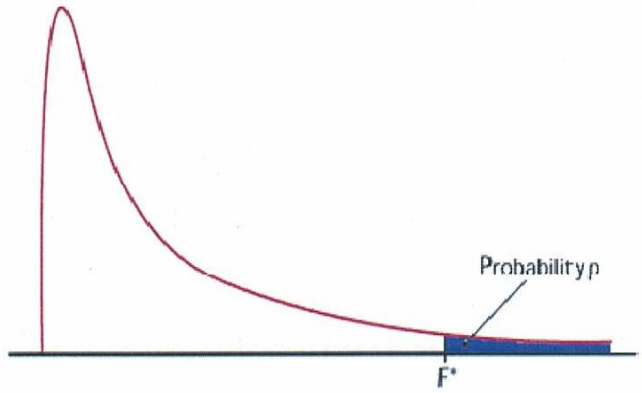


Figure 5 2 F-distribution with p value and corresponding f value

The large data set for the SRC willow has been statistically analysed and two types of statistical analysis has been used:

1. *Analysis of Variance* (ANOVA) is used to look at any differences between treatments, sampling times or interaction between treatments and sampling times for the fuel characteristics and;
2. *Regression Analysis* is used to look at the correlation between volatile combustion peak temperatures from TGA combustion and certain metals concentration.

5.4 Fuel Characterisation.

The fuels have been characterised as in Section 5.2 and statistically analysed using ANOVA to get an initial conclusion on which treatment and which sampling time would be the most desirable to achieve optimum fuel quality.

5.4.1 Analysis of Variance (ANOVA)

ANOVA provides a general framework for the testing of hypothesis and the estimation of treatment means or comparisons between treatment means with variance and standard errors. It also allows incorporation of the structure of the experimental design in the analysis. The total variation between the observations on the experimental units is divided into components (blocking, treatment etc.) and these are compared to see if there is any significant variation between the units other

than that attributed to background variation. ANOVA with repeated measurements is used in this study to be able to look at differences between sampling times as well. Whole different trees are sampled at each sampling time. This is overlooked here since all the trees are from the same plot.

5.4.2 Application of ANOVA to the SRC willow experiment

Since the SRC willow experiment is a Randomised Complete Block Design (RCBD), the differences between blocks (biological and environmental) and treatments are considered as the background and sample variations respectively. Errors made in the laboratory measurements (when measuring ash contents, nitrogen contents etc) are not taken into account. ie these errors are assumed to be low compared to the variation between samples.

The statistical analysis is split into 4 groups where a combination of different treatments is analysed together in order to examine the effect of nitrogen, potassium, sulphur and sewage pellets. Treatments A, D and F examine, the nitrogen effect (N effect), treatments A, D and J examine the potassium effect (K effect), treatments A, D and N examine the sulphur effect (S effect) while all 6 treatments are used to examine the effect of sewage pellets (SP effect).

ANOVA tables were generated using Genstat and comparisons were made between treatments, sampling times and interaction between treatments and sampling time. The *F probabilities* (Fpr), *Standard Error of an estimated Difference* between treatments (SED) and *Least Significant Difference* (LSD) have been reported.

- **Fpr** is the probability of the F distribution. A critical probability level of 0.05 (most commonly used in statistics) has been chosen for the analysis. Genstat can compute exact Fpr values, instead of giving a pre-determined critical value, in all cases except when the Fpr is less than 0.001 in which case it is reported as <0.001. For this study, only significant results (Fpr $\leq$ 0.05) for differences between treatments, sampling time and their interaction) have been discussed.

- **SED** is a measure of the uncertainities in the estimate of a treatment difference and is calculated according to Equation 5.2

$$SED = \sqrt{s^2\left(\frac{1}{n_1}+\frac{1}{n_2}\right)} \qquad \text{Equation 5.2}$$

where s^2 is the sample variance calculated from the replicates for each treatment and n_1 and n_2 are the number of replicates for treatments 1 and 2 respectively.

- **LSD** is the smallest difference between means that would result in statistical significance is calculated as in Equation 5.3

$$LSD = t_\alpha \times SED \qquad Equation\ 5.3$$

where t_α is the 100(1-α) % tabulated value of the student's t-distribution with the residual degrees of freedom . The value of α is taken as 0.05.

5.5 Results and Discussion of ANOVA for Fuel Characterisation

The results of all the fuel characterisation are discussed in this section. Tables of treatment means, ANOVA tables and graphs are illustrated here and significant results have been discussed for the basic fuel properties. The individual results for proximate and ultimate analysis on and the calculated CVs on a dry basis (db) for each individual plot for each treatment are shown in Appendix B. The metal analyses received from Rothamsted Research are listed in Appendix C, while their corresponding calculated ash compositions and slagging and fouling indices are listed in Appendix D.

The ANOVA analyses are split into 3 groups showing; treatment differences (Treatment), sampling time differences (Time) and the differences in the interaction of treatment and sampling times (Treatment.Time). A confidence interval of 95% with an F probability of 0.05 ($Fpr_{0.05}$) has been used for the ANOVA calculations. An Fpr of ≤0.05 indicates at least one treatment or sampling time is significantly different from the others. To identify which treatment, sampling time or interaction between the treatment and sampling time are different, the LSDs are examined and the results are interpreted as follows:

- For F probabilities >0.05 it can be concluded that there are no significant differences while F probabilities ≤0.05 show at least one significant difference. For example from the ANOVA table for carbon (Table 5.4), it is seen that there is a significant

difference between sampling times for leaves for the N effect since the F probability Fpr = 0.002.

- For Fpr ≤0.05, the LSDs are compared with the treatment means to identify the differences between treatment, sampling time or interaction between treatment and sampling time. For the above example the LSD for the N effect on leaves for the carbon content is 0.615. This value is subtracted from 50.22 (mean for treatment A for the 1st sampling time) to give 49.61 which is then compared with the means of treatment A for Sep-08 and Oct-09, and means of treatments D and F for all three sampling times.. In this example, it is found that the carbon content is highest in Oct-07 for all three treatments. Differences between treatments can be examined in a similar way.
- In some cases, where the LSDs are compared with treatment means, the differences are not obvious and hence SEDs are compared to interpret the results and obtain conclusions.

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5.5.1 Carbon Content (% db)

The carbon content of different types of biomass varies with many agricultural residues having the highest carbon contents (~49-55 wt % db) followed by woody biomass (~ 47.1-52.5 wt % db) and herbaceous biomass having the lowest carbon content (~ 43.2-50.7 wt % db) (Loo and Koppejan, 2008).

Table 5 3 Treatment means of carbon content (% db) for all sampling times

Treatment	Leaves			Stems					
	Oct-07	Sep-08	Oct-09	Oct-07	Mar-08	Sep-08	Mar-09	Oct-09	Jan-10
A	50.22	49.50	48.99	50.73	51.62	48.90	48.04	48.29	49.58
D	49.93	49.61	48.19	48.57	50.03	49.63	48.25	48.27	47.52
F	49.98	48.97	48.98	49.56	48.81	48.54	48.35	49.02	48.52
J	49.26	50.64	50.79	47.96	47.60	45.58	45.79	49.29	50.85
N	47.20	50.26	50.91	50.78	48.16	49.41	48.31	48.45	48.97
O	46.64	46.45	47.58	50.95	48.62	45.44	45.21	45.80	45.81

*Refer to Table 5.1 for the fertilizer treatment details.

Table 5.3 shows the treatment means for all the sampling times for leaves and stems this data is also plotted in Figure 5.3 and Figure 5.4 to show the trends more clearly. The treatment means vary from 45.21 to 50.91 wt% (db). ANOVA calculations can establish if any of the differences in the treatment means are significant and the parameter and from the ANOVA calculations are shown in Table 5.4.

Table 5 4 ANOVA parameters for treatment means of carbon content (% db)

		Leaves			Stems		
		SED	LSD	$Fpr_{0.05}$	SED	LSD	$Fpr_{0.06}$
N effect	Treatment	0.581	1.613	0.843	0.531	1.475	0.343
Treatments	Time	0.277	0.615	**0.002**	0.454	1.086	**0.016**
A, D, F	Treatment.Time	0.700	1.635	0.380	0.894	2.112	0.106
K effect	Treatment	0.571	1.585	0.318	1.135	4.263	0.592
Treatments	Time	0.281	0.657	0.140	1.099	2.926	0.306
A, D, J	Treatment.Time	0.695	1.662	**0.009**	2.318	5.947	0.341
S effect	Treatment	1.000	2.777	0.947	0.592	1.642	0.454
Treatments	Time	0.732	1.668	0.629	0.772	1.931	0.167
A, D, N	Treatment.Time	1.440	3.221	0.077	1.357	3.320	0.406
Sewage pellets	Treatment	1.112	2.479	0.146	1.018	2.268	0.240
effect	Time	0.828	1.758	0.853	1.047	2.515	0.268
All treatments	Treatment.Time	1.995	4.156	0.768	2.554	6.069	0.828

From examination of Tables 5.3 and 5.4 and Figures 5.1 and 5.2, a few significant conclusions can be drawn as discussed below.

5.5.1.1 Treatment Differences for carbon content (% db)

There are no significant treatment differences in the carbon content for either leaves or stems for the N. K, S or Sewage pellets effects since all of them have Fpr >0.05.

5.5.1.2 Sampling Time Differences for carbon content (% db)

For the effect of N fertiliser, there is a significant difference between sampling times for both leaves (Fpr = 0.002 and LSD = 0.615) and stems (Fpr = 0.016 and

LSD = 1.086). For the leaves it is seen that Oct-07 has the highest carbon content which decreases through to Oct-09 for all the treatments except in the case of the sample taken in Sep-08 for treatment F (see Table 5.3). For the stems, samples taken in Oct-07 and Mar-08 have higher carbon contents compared to the other 4 sampling times. For treatments A and D, carbon contents increase from Oct-07 to Mar-08 and then decrease from Mar-08 to Mar-09. For treatment A, the C content increases from Mar-09 to Jan -10; for treatment D increases are similar to this until Oct-09 and then decrease. For treatment F, carbon content decreases from Oct-07 to Mar-09 and then increases from Mar-09 to Oct-09 and then decreases again. The differences between the influence of sampling times on carbon content are greater for the stems than for the leaves as illustrated in Figures 5.3a and 5.3d respectively. These figures illustrate the influence of N fertiliser on C content. Notice that the SED value for which stems (SED = 0.454) is higher compared to that for leaves (SED = 0.277). Treatment F seems to have the opposite effect on C content compared to the other two treatments used to study the N effect. The application of nitrogen fertilizer on its own does not seem to have an impact on the carbon content of the willow.

5.5.1.3 Interactions for carbon content (% db)

A significant difference in the interaction of treatment and sampling time is seen for the leaves for the effect of K fertiliser (Fpr = 0.009 and LSD = 1.662 in Table 5.4). It is seen that there is a decrease in C content in leaves from Oct-07 to Oct-09 for treatments A and D but an increase of C content in leaves for treatment J over the same time period. Treatment J also has a higher C content compared to A and D. This high C content in Treatment J could possibly be due to the result of adding both potassium and nitrogen as the fertilizer.

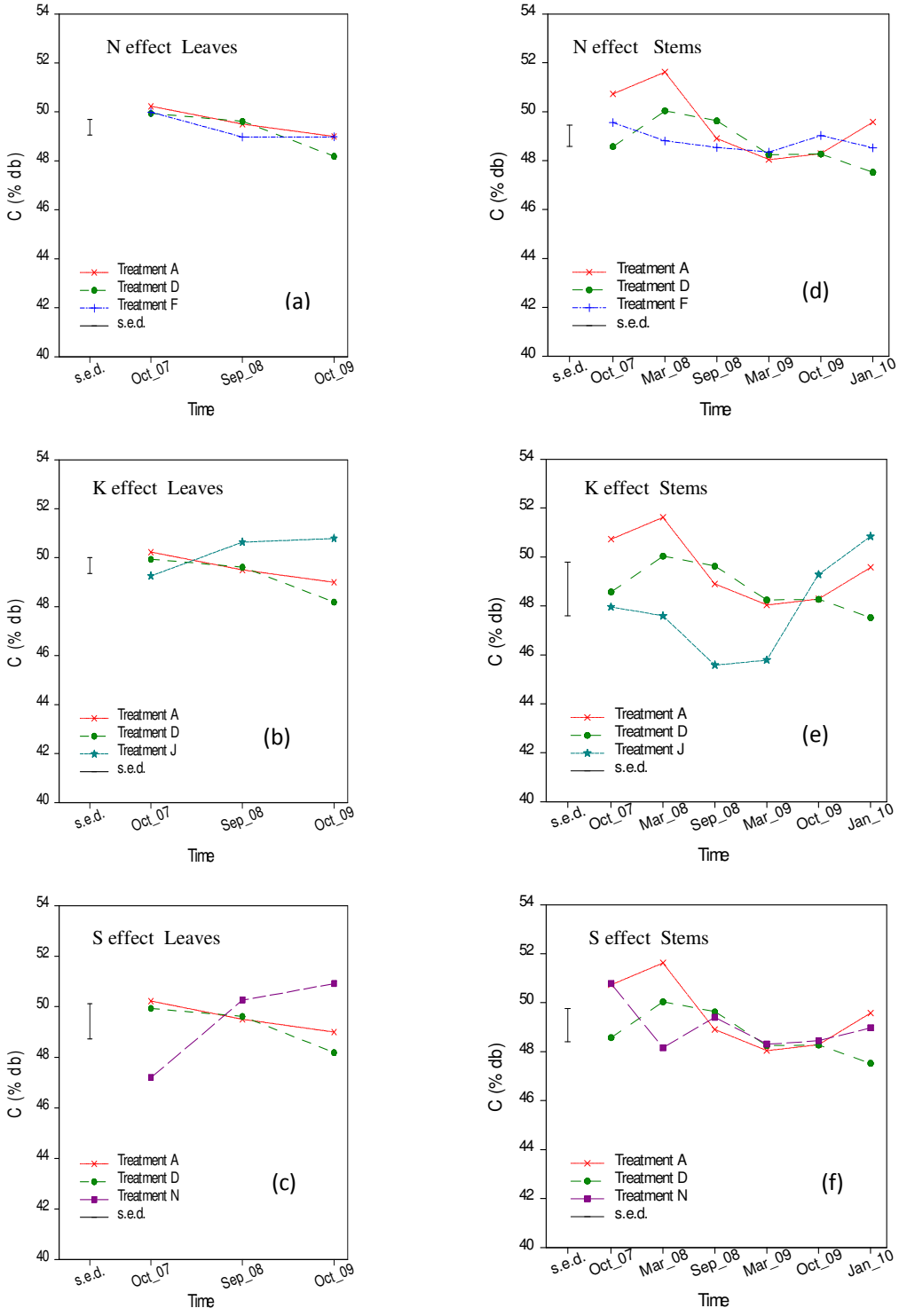


Figure 5 3 Treatment means with sampling time of caarbon content (% db) for leaves (a-c) and stems (d-f) for the N, K and S effect respectively

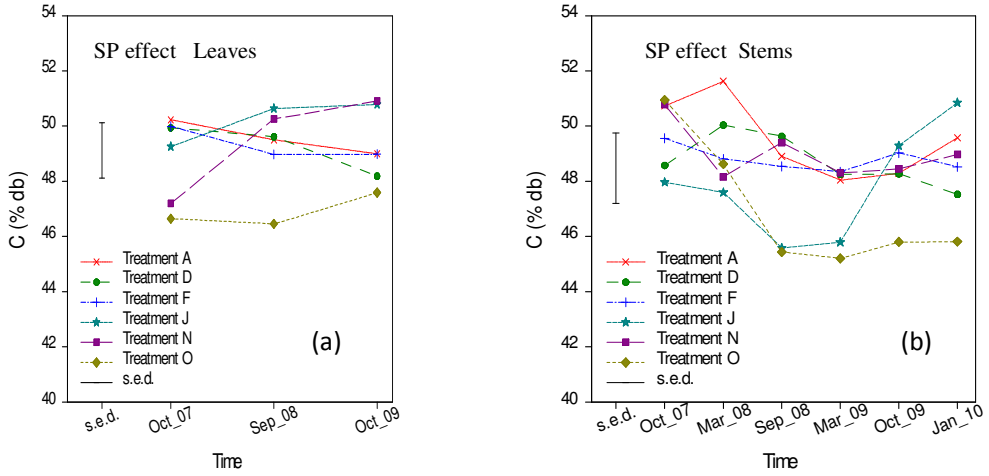


Figure 5 4 Treatment means with sampling time of caarbon content (% db) for leaves (a) and stems (b) for the sewage pellets effect

5.5.2 Nitrogen Content (% db)

The nitrogen content in biomass can vary from 0.1-12% on a dry ash free (daf) basis. Animal biomass like chicken litter have the highest nitrogen contents (~ 6.2-12.2%) while wood and woody biomass have the lowest nitrogen contents (~0.1-0.7%) (Vassilev et al., 2010).

Table 5 5 Treatment means of nitrogen content (% db) for all sampling times

Treatment	Leaves			Stems					
	Oct-07	Sep-08	Oct-09	Oct-07	Mar-08	Sep-08	Mar-09	Oct-09	Jan-10
A	1.88	2.61	2.12	0.05	0.09	0.35	0.45	0.32	0.27
D	2.07	2.53	1.72	0.07	0.20	0.38	0.37	0.30	0.23
F	2.04	2.63	2.07	0.14	0.07	0.43	0.41	0.67	0.33
J	2.23	3.05	2.28	0.50	0.47	0.45	0.58	0.55	0.55
N	2.15	2.53	2.56	0.54	1.50	0.40	0.42	0.72	1.12
O	0.41	2.56	2.14	0.49	1.67	0.44	0.62	0.26	0.22

Table 5.5 and Figures 5.5 and 5.6 shows the treatment means for nitrogen with sampling time. The nitrogen contents of the leaves (0.41-3.05 wt% db) of SRC willow are higher than those of stems (0.05-1.67 wt% db). The ANOVA

calculations can establish if any differences in the treatment means are significant and the ANOVA results are shown in Table 5.6.

Table 5 6 ANOVA parameters for treatment means of nitrogen content (% db)

		Leaves			Stems		
		SED	LSD	$Fpr_{0.05}$	SED	LSD	$Fpr_{0.06}$
N effect	Treatment	0.233	0.648	0.828	0.050	0.138	0.258
Treatments	Time	0.090	0.229	**<0.001**	0.053	0.131	**<0.001**
A, D, F	Treatment.Time	0.266	0.682	0.232	0.098	0.235	0.169
K effect	Treatment	0.139	0.385	0.083	0.029	0.081	**0.001**
Treatments	Time	0.135	0.323	**0.002**	0.082	0.216	0.133
A, D, J	Treatment.Time	0.235	0.539	0.458	0.133	0.347	0.619
S effect	Treatment	0.120	0.333	0.132	0.102	0.284	**0.010**
Treatments	Time	0.146	0.379	**0.033**	0.156	0.407	0.283
A, D, N	Treatment.Time	0.239	0.582	0.222	0.267	0.681	0.134
Sewage pellets	Treatment	0.212	0.472	**0.039**	0.102	0.226	**0.002**
effect	Time	0.098	0.215	**<0.001**	0.108	0.257	0.109
All treatments	Treatment.Time	0.289	0.621	**<0.001**	0.263	0.617	**0.022**

5.5.2.1 Treatment Differences for nitrogen content (% db)

There are significant differences between treatments for the N-content of leaves (Fpr = 0.039 and LSD = 0.472) with the application of sewage pellets. All the treatments show a similar trend where the N content increases from Oct-07 to Oct-08 and then decreases from Oct-08 to Oct-09. Treatment J has the highest N content. Significant differences in N-content of stems between treatments are seen for the K effect (Fpr = 0.001 and LSD = 0.081), S effect (Fpr = 0.01 and LSD = 0.284) and sewage pellets effect (Fpr = 0.002 and LSD = 0.226). For the K and S effects, treatment J and N have the highest N contents respectively. This indicates that nitrogen fertilizer on its own does not impact the nitrogen in the fuel but the addition of potassium or sulphur to the nitrogen fertilizer enhances the uptake of nitrogen in the fuel. For the sewage pellets effect, treatment J has the highest nitrogen content while treatment D has the lowest nitrogen content except for the Oct-07 sample for which treatment O has the lowest nitrogen content.

5.5.2.2 Sampling Time Differences for nitrogen content (% db)

There are significant differences between sampling times for leaves for the N effect (Fpr = <0.001 and LSD = 0.229), K effect (Fpr = 0.002 and LSD = 0.323), S effect (Fpr = 0.033 and LSD = 0.379) and sewage pellets effect (Fpr = <0.001 and LSD = 0.251). All the treatments show a similar trend with Sep-08 having the highest nitrogen content as illustrated in Figures 5.5 and 5.6. For the stems, the N effect (Fpr = <0.001 and LSD = 0.131) has a significant difference. The nitrogen content of stems receiving treatment A increases form Oct-07 to Mar-09 and then decreases, while for those receiving treatment D the N-content increases from Oct-07 to Sep-08 and then decreases. For those receiving treatment J the nitrogen content decreases from autumn to spring samples and on the whole increases from the 1st to 3rd year of maturity.

5.5.2.3 Interactions for nitrogen content (% db)

The application of sewage pellets shows a significant difference in nitrogen content for both leaves and stems when the interaction of treatment and sampling time is considered (Table 5.5 and Figure 5.6). For the leaves, all the treatments follow a similar trend but there is some scatter on the treatment means, such that the treatment with the highest nitrogen content for one sampling time does not necessarily have the highest nitrogen content for the other sampling times and vice versa. For the stems, the trends are not similar for all the treatments. Treatments A and D respond similarly with nitrogen content increasing from Oct-07 to Sep-08 and Oct-07 to Mar-09 for treatments A and D respectively. Treatments F and J behave very differently to the other treatments. Nitrogen content of treatment J decreases from Oct-07 to Sep-08 with a sharp increase from Sep-08 to Mar-09 and then remains almost steady. The nitrogen contents of treatment F decrease from samples taken in autumn to those taken in spring. For treatments N and O, the nitrogen contents in the fuels increase from samples taken in autumn to those taken in spring except for the third year for treatment O in which case the nitrogen content decreases from autumn to spring.

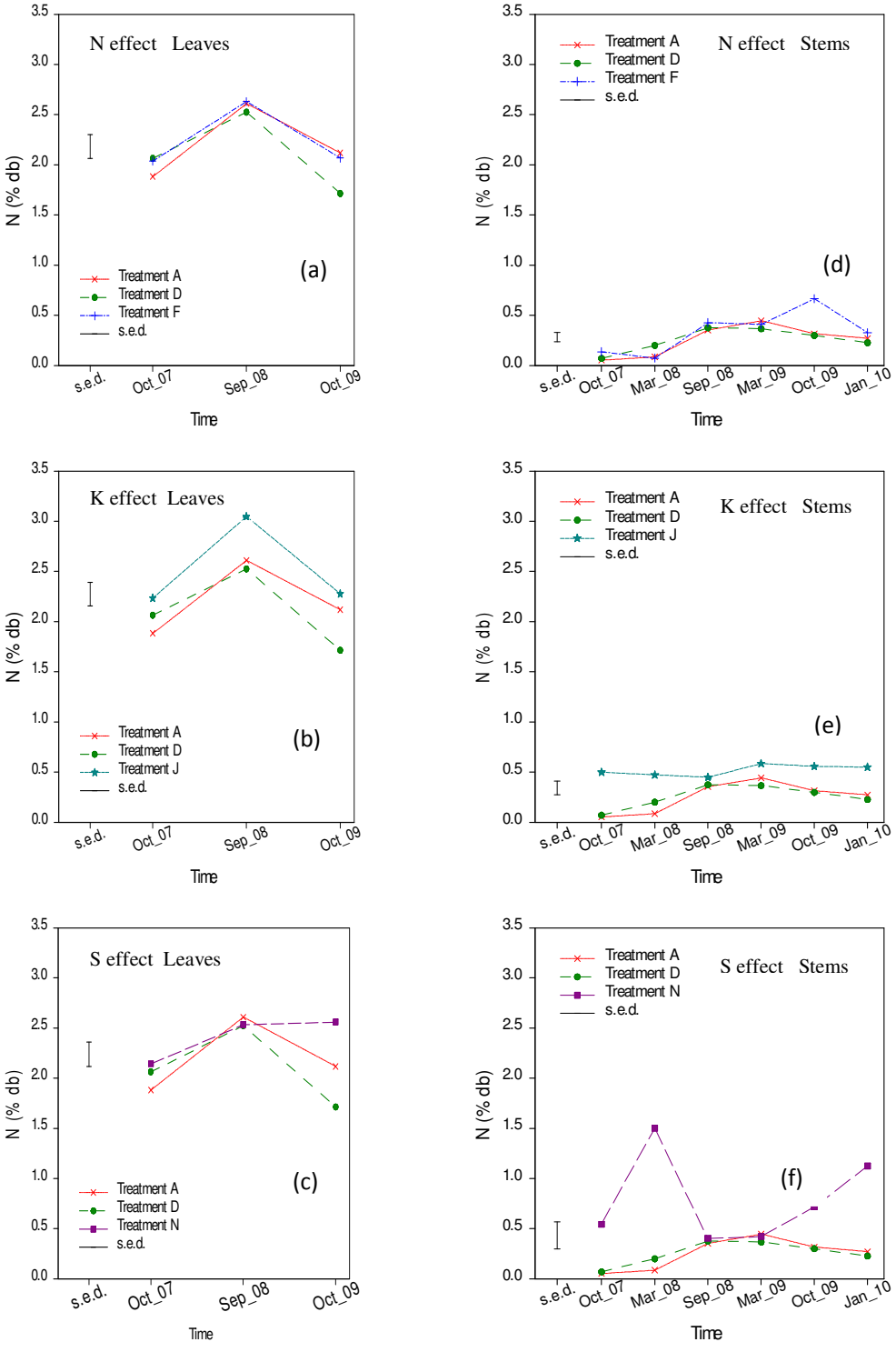


Figure 5 5 Treatment means with sampling time of nitrogen content (% db) for leaves (a-c) and stems (d-f) for the N, K and S effect respectively

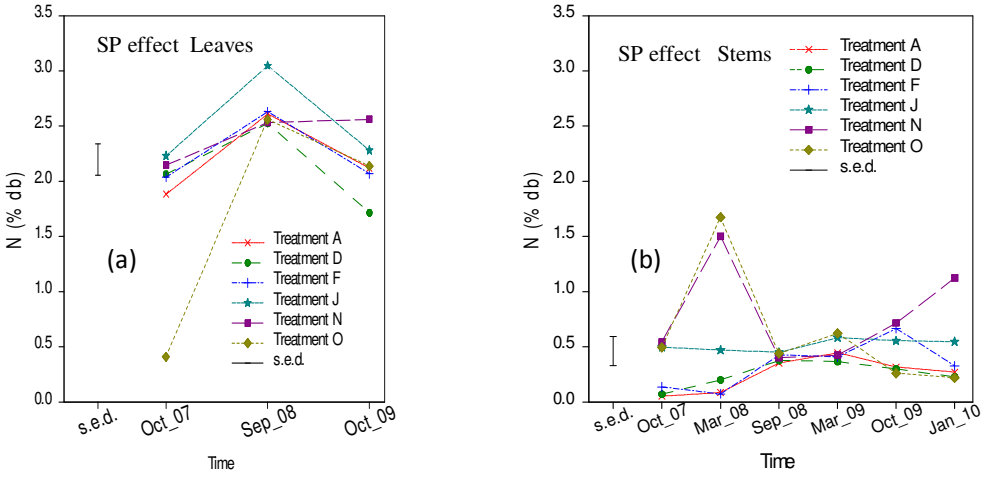


Figure 5 6 Treatment means with sampling time of nitrogen content (% db) for leaves (a) and stems (b) for the sewage pellets effect

5.5.3 Calorific Value (CV MJ/Kg)

The CV of a fuel is the enthalpy of complete combustion of the fuel where all the carbon is converted to CO_2 and all the hydrogen is converted to H_2O. CVs are of two types; Gross Calorific Value (GCV) and Net Calorific Value (NCV) the latter of which does not include the condensation enthalpy of water while the former does (Friedl et al., 2005). Fuels with high C contents have higher CVs. The CVs of biomass are usually in the range of 18 – 22MJ/Kg with some agricultural residues and woody biomasses having higher CVs compared to herbaceous biomass (Loo and Koppejan, 2008). In this study, only the GCVs are reported.

Table 5 7 Treatment means of CVs (MJ/Kg db) for all sampling times

Treatment	Leaves			Stems					
	Oct-07	Sep-08	Oct-09	Oct-07	Mar-08	Sep-08	Mar-09	Oct-09	Jan-10
A	20.41	20.21	19.76	20.27	20.67	19.44	19.06	19.18	19.62
D	20.37	20.18	19.33	19.37	20.04	19.88	19.18	19.14	18.86
F	20.40	19.88	19.75	19.85	19.29	19.38	19.30	19.55	19.26
J	19.83	20.85	20.68	18.90	18.75	18.42	18.49	19.57	20.33
N	19.04	20.43	20.77	20.35	19.23	19.64	19.21	19.24	19.55
O	18.51	19.13	19.15	20.63	19.46	18.32	18.29	18.13	18.12

From the treatment means listed in Table 5.7, it can be seen that theCVs of SRC willow are in the ranges of 18-21MJ/Kg. The CVs are very similar for leaves and stems since the C contents of the stems and leaves are also very similar. Table 5.8 shows the ANOVA results which examines the significance between the data in Table 5.6. The data in Table 5.7 is also plotted in figures 5.7 and 5.8 so that trends can be seen more easily.

Table 5 8 ANOVA parameters for treatment means of CVs (MJ/KG db)

		Leaves			Stems		
		SED	LSD	$Fpr_{0.05}$	SED	LSD	$Fpr_{0.06}$
N effect	Treatment	0.496	1.106	0.137	0.381	0.848	0.291
Treatments	Time	0.352	0.739	0.594	0.421	0.998	0.271
A, D, F	Treatment.Time	0.862	1.777	0.566	0.015	2.387	0.759
K effect	Treatment	0.297	0.825	0.337	0.588	1.633	0.604
Treatments	Time	0.159	0.387	0.052	0.411	1.071	0.327
A, D, J	Treatment.Time	0.373	0.897	**0.013**	0.877	2.223	0.242
S effect	Treatment	0.479	1.330	0.937	0.269	0.746	0.588
Treatments	Time	0.357	0.808	0.568	0.350	0.876	0.140
A, D, N	Treatment.Time	0.696	1.547	0.074	0.615	1.506	0.442
Sewage pellets	Treatment	0.315	0.875	0.867	0.236	0.655	0.457
effect	Time	0.142	0.326	**0.001**	0.213	0.498	**0.015**
All treatments	Treatment.Time	0.374	0.895	0.375	0.411	0.953	0.088

5.5.3.1 Treatment Differences for CVs (MJ/KG db)

There are no significant differences in the CVs of either leaves or stems as a result of different treatments. All of them have Fpr >0.05. From the SEDs listed in Table 5.8, it is more evident that there is more variation in the CVs of leaves compared to stems for the N, S and sewage pellet effects while more variation in the CVs of stems compared to leaves is evident for the K effect.

5.5.3.2 Sampling Time Difference for CVs (MJ/KG db)

There are significant differences between CVs of both leaves (Fpr = 0.001 and LSD = 0.326) and stems (Fpr = 0.015 and LSD = 0.498) as a result of sampling times but only for the sewage pellets effect. For the leaves, Trestments A, D and F show a decrease in CV from Oct-07 to Oct-09 while Treatments N and O show an

increase in CV from Oct-07 to Oct-09. Treatment J behaves differently with an increase in CV from Oct-07 to Sep-08 and a decrease in CV from Sep-08 to Oct-09. For the stems, the CVs do not follow a particular trend throughout the 3 year cycle but from the SEDs it can be concluded that stems (SED = 0.213) have more variation compared to leaves (SED = 0.142).

5.5.3.3 Interactions for CVs (MJ/KG db)

According to the statistics, there is a significant difference for the interaction of treatment and sampling time for leaves for the K effect. Treatment J has a slightly lower and slightly higher CV for the Oct-07 and Sep-08 to Oct-09 samples respectively compared to Treatments A and D. Treatment J also behaves differently with sampling times with Sep-08 having higher CVs compared to Oct-07 and Oct-09. Treatments A and D show a decrease in CV from Oct-07 to Oct-09. The interaction between treatment and sampling time for CV shows a very similar trend to that of the C content in section 5.4.1.1 indicating that the CV is highly dependant on the C content of the fuel.

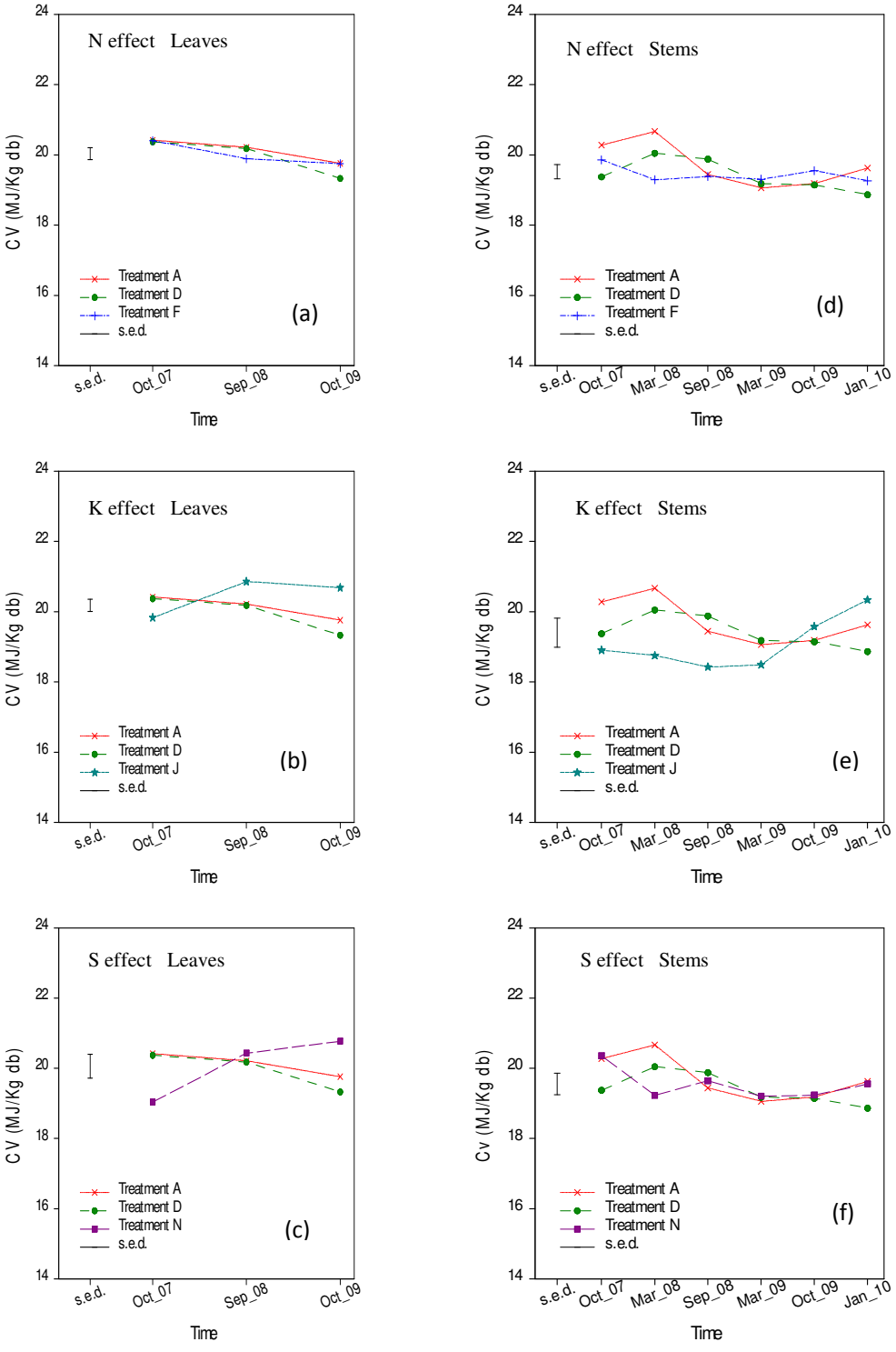


Figure 5 7 Treatment means with sampling time of Calorific Value (MJ/Kg db) for leaves (a-c) and stems (d-f) for the N, K and S effect respectively

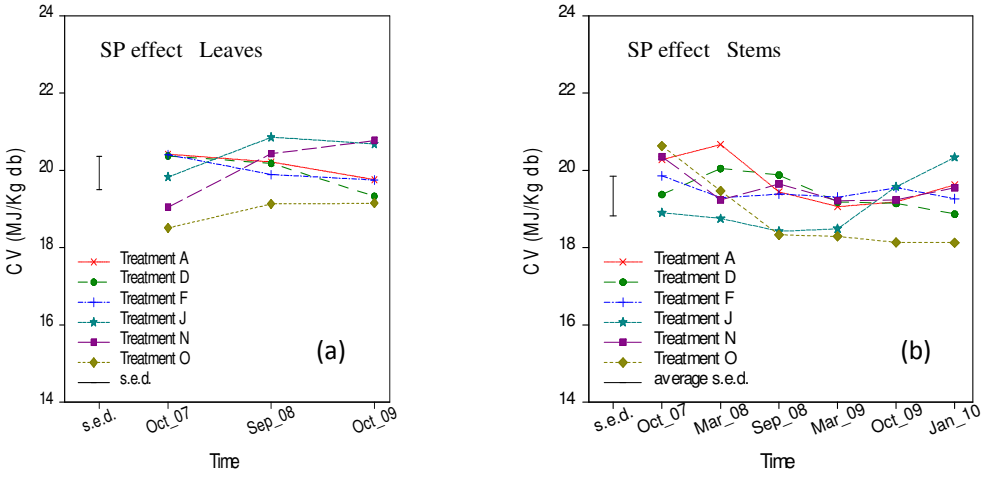


Figure 5 8 Treatment means with sampling time of Calorific Value (MJ/Kg db) for leaves (a) and stems (b) for the sewage pellets effect

5.5.4 Ash (% db)

Fuels with high ash contents are less desirable for use in power stations compared to those with lower ash contents. Ash contents of biomass may vary from 0.5-12 wt% (db) with woody biomass (0.5-2.5 wt%) having low ash contents and cereals and straws (4-12 wt%) having high ash contents (Loo and Koppejan, 2008).

Table 5 9 Treatment means of ash content (% db) for all sampling times1`

Treatment	Leaves			Stems					
	Oct-07	Sep-08	Oct-09	Oct-07	Mar-08	Sep-08	Mar-09	Oct-09	Jan-10
A	6.08	7.29	8.31	1.76	0.66	0.85	1.34	1.12	1.08
D	6.49	7.20	8.30	0.88	1.41	0.92	1.29	1.02	0.99
F	6.27	8.13	7.58	1.11	0.77	1.31	1.33	0.90	0.95
J	6.08	7.29	8.04	0.93	0.89	1.26	1.41	0.96	0.87
N	6.95	6.93	7.61	1.05	0.87	1.07	1.28	0.83	0.94
O	6.46	7.56	7.49	0.82	0.90	1.11	1.26	0.79	0.77

Table 5.9 shows the treatment means of ash contents for leaves and stems for the different sampling times. Leaves (6.08-8.3 %) have much higher ash contents compared to stems (0.66-1.76%). Table 5.10 shows the ANOVA results for the ash

contents. The data in Table 5.9 is also presented in Figures 5.9 and 5,10 where trends can be observed more clearly

Table 5 10 ANOVA parameters for treatment means of ash content (%db)

		Leaves			Stems		
		SED	LSD	$Fpr_{0.05}$	SED	LSD	$Fpr_{0.06}$
N effect	Treatment	0.164	0.455	0.801	0.131	0.363	0.251
Treatments	Time	0.272	0.705	**0.003**	0.168	0.421	0.245
A, D, F	Treatment.Time	0.418	1.036	0.196	0.296	0.726	0.191
K effect	Treatment	0.102	0.284	0.286	0.130	0.362	0.231
Treatments	Time	0.088	0.205	**<0.001**	0.169	0.428	0.208
A, D, J	Treatment.Time	0.161	0.363	0.137	0.298	0.736	0.234
S effect	Treatment	0.144	0.399	0.563	0.151	0.420	0.243
Treatments	Time	0.103	0.246	**<0.001**	0.165	0.406	0.167
A, D, N	Treatment.Time	0.205	0.472	**0.003**	0.302	0.726	0.297
Sewage pellets	Treatment	0.146	0.326	0.665	0.107	0.238	**0.024**
effect	Time	0.159	0.354	**<0.001**	0.092	0.222	**0.090**
All treatments	Treatment.Time	0.350	0.764	0.051	0.233	0.552	0.141

5.5.4.1 Treatment Differences for Ash (% db)

Significant differences between ash content as a result of different fertiliser treatments are only seen for the stems for the sewage pellets effect. The ash contents for all the treatments are scattered over a narrow range. The only points which are significantly different are the stems from Oct-07 and Mar-08 samples for Treatments A and D respectively since these two ash contents are much higher compared to the samples for other treatments at these 2 sampling times. Thus we can conclude that fertiliser treatment alone does not influence ash content of SRC willow unless sewage pellets are applied, then lower ash may result.

5.5.4.2 Sampling Time Differences for Ash (% db)

The ash content of SRC willow leaves varies over the maturity period. The ash content generally increases from Oct-07 to Oct-09 for all the treatments except Treatments F and O in which case the ash content increases from Oct-07 to Sep-08 and then decreases from Sep-08 to Oct-09. For stems, a significant difference is seen for the sewage pellets effect. The ash content decreases from Oct-07 to Mar-08

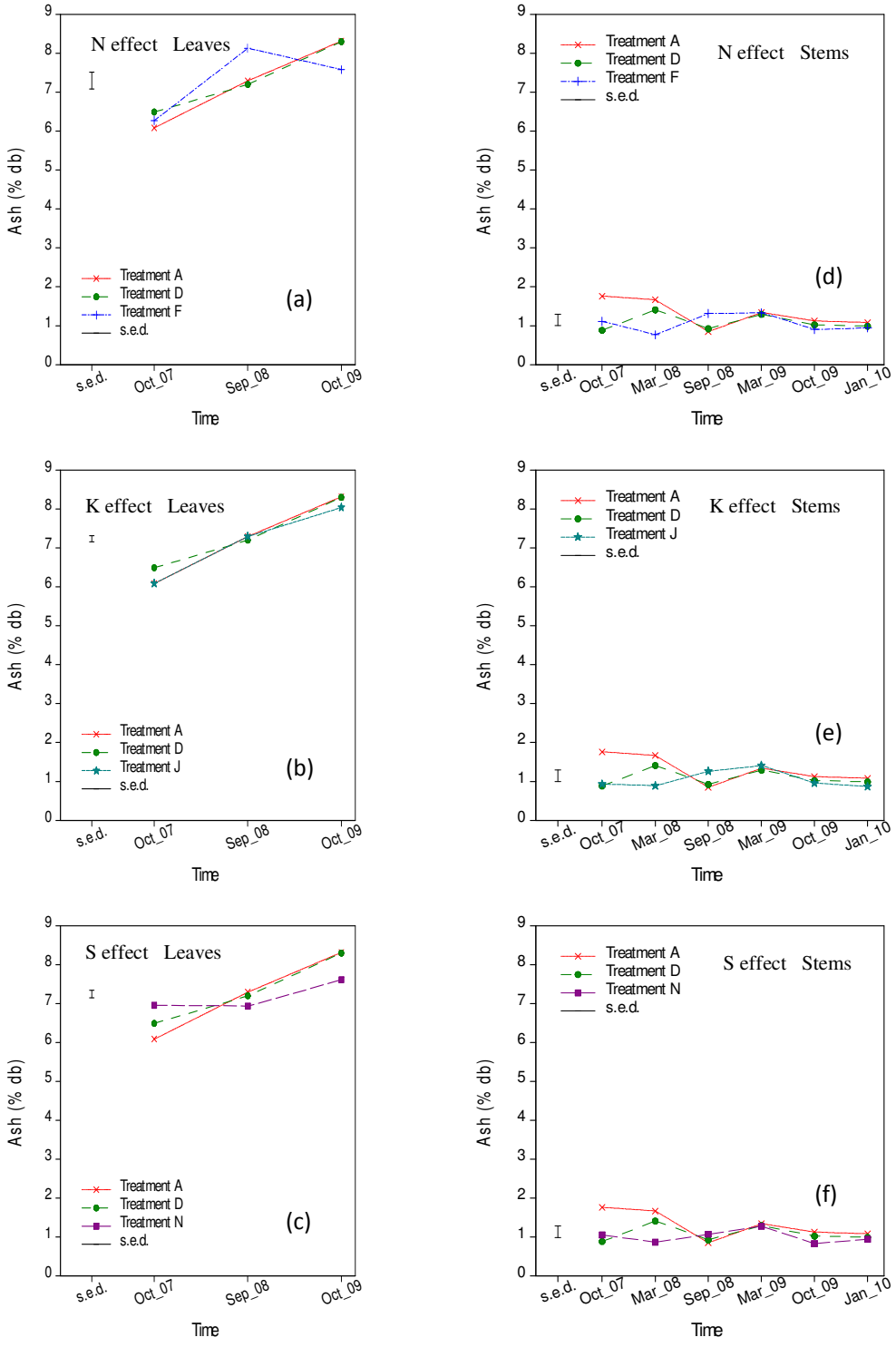


Figure 5 9 Treatment means with sampling time of ash content (db) for leaves (a-c) and stems (d-f) for the N, K and S effect respectively

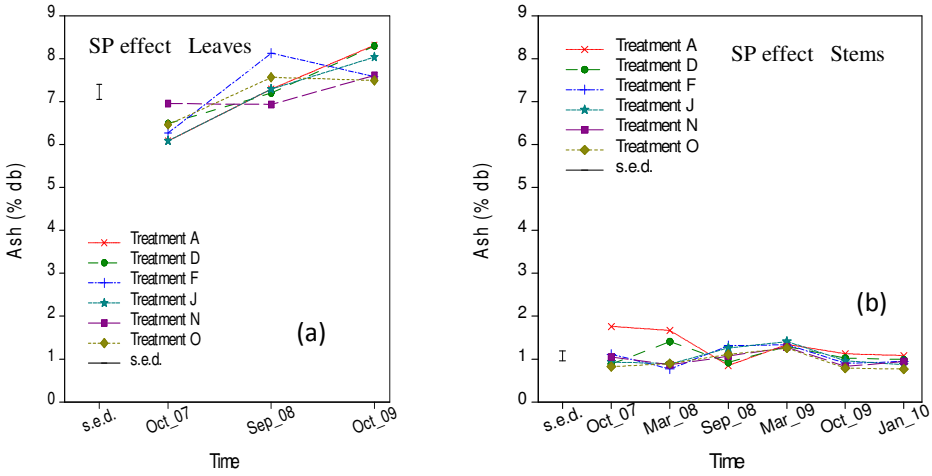


Figure 5 10 Treatment means with sampling time of ash content (db) for leaves (a) and stems (b) for the sewage pellets effect

for all treatments except Treatments D and O and then the ash content increases from Sep-08 to Mar-09 for all the treatments and then it decreases again from Oct-09 to Jan-10 for all treatments except Treatments F and N. In conclusion, the optimum harvest time is spring to achieve low ash contents.

5.5.4.3 Interactions for Ash (% db)

There is an interaction between treatment and sampling time for the S effect in which case the ash content increases from Oct-07 to Oct-09 for Treatments A and D and it remains stable from Oct-07 to Sep-09 and then increases from Sep-08 to Oct-09 for Treatment N.

5.5.5 Ash Composition

Biomass is composed of inorganic metals including K, Na, Ca, Mg, P, S, Fe, Al, Ti, Si and Mn and some heavy metals such as Cd, Cu, Pb and so on (Jenkins et al., 1998). During the combustion process, ash is formed which is composed of oxides, chlorides, sulphates, carbonates and phosphates of theses inorganic metals (Bryers, 1996). It is some of these metal components in the ash that influence the operability, efficiency and lifetime of the furnaces and boilers in power plants

For the SRC willow the metals in the fuel were analysed via ICP as described in Section 3.3.6 and the ash composition was then calculated using these metal analyses. It has been assumed that all the metals in the ash are in the form of stable oxides. The ash composition was calculated as follows, For example Equation 5.4 is used to calculate K_2O as a weight percent.

$$wt\%\ K_2O = \frac{\left(\left(\frac{K\ (ppm)}{2 \times 39.1}\right) \times (39.1 + 39.1 + 16)\right)}{\left(10^4 \times wt\ \%\ ash\ (db)\right)} \qquad Equation\ 5.4$$

where 39.1 and 16 are the atomic masses of K and O respectively.

The ash components calculated for the SRC willow are Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, Mn_3O_4, Na_2O, P_2O_5, SO_3, TiO_2 and SiO_2. The latter was measured from its ash for a subset of the samples since ample sample was not available.. These components are good representatives of biomass ash. The ash components of SRC willow have been split into two groups, the most abundant (major metals) and the least abundant (minor metals). The treatment means of the major and minor metals are illustrated in Figures 5.11, 5,12 and 5.13, 5.14 respectively for leaves and stems for all the treatments over all sampling times.

5.5.5.1 Major Metals

The major metals consist of CaO, K_2O, P_2O_5, SO_3 and MgO. CaO, K_2O, P_2O_5 make up almost 80%. In some of the cases, major metals make up more than 100% of the ash. This is because it has been assumed that the ash is made up of stable oxides only which may not necessarily be the case. Some of the inorganic metals may also be converted to chlorides, sulphates carbonates or phosphates, hence there might be an overestimation of oxygen based components (Seminar et al., 2009). This is particularly the case for the stems. The measured SiO_2 ranges from 2-11% as reported in Table 5.21 later and can also be considered a major metal. SRC willow can be considered a high calcium, high potassium, low silica biomass (Bryers, 1996) with respect to slagging, fouling and ash melting as will be seen in Section 5.5.6. Stems have higher major metals content compared to leaves.

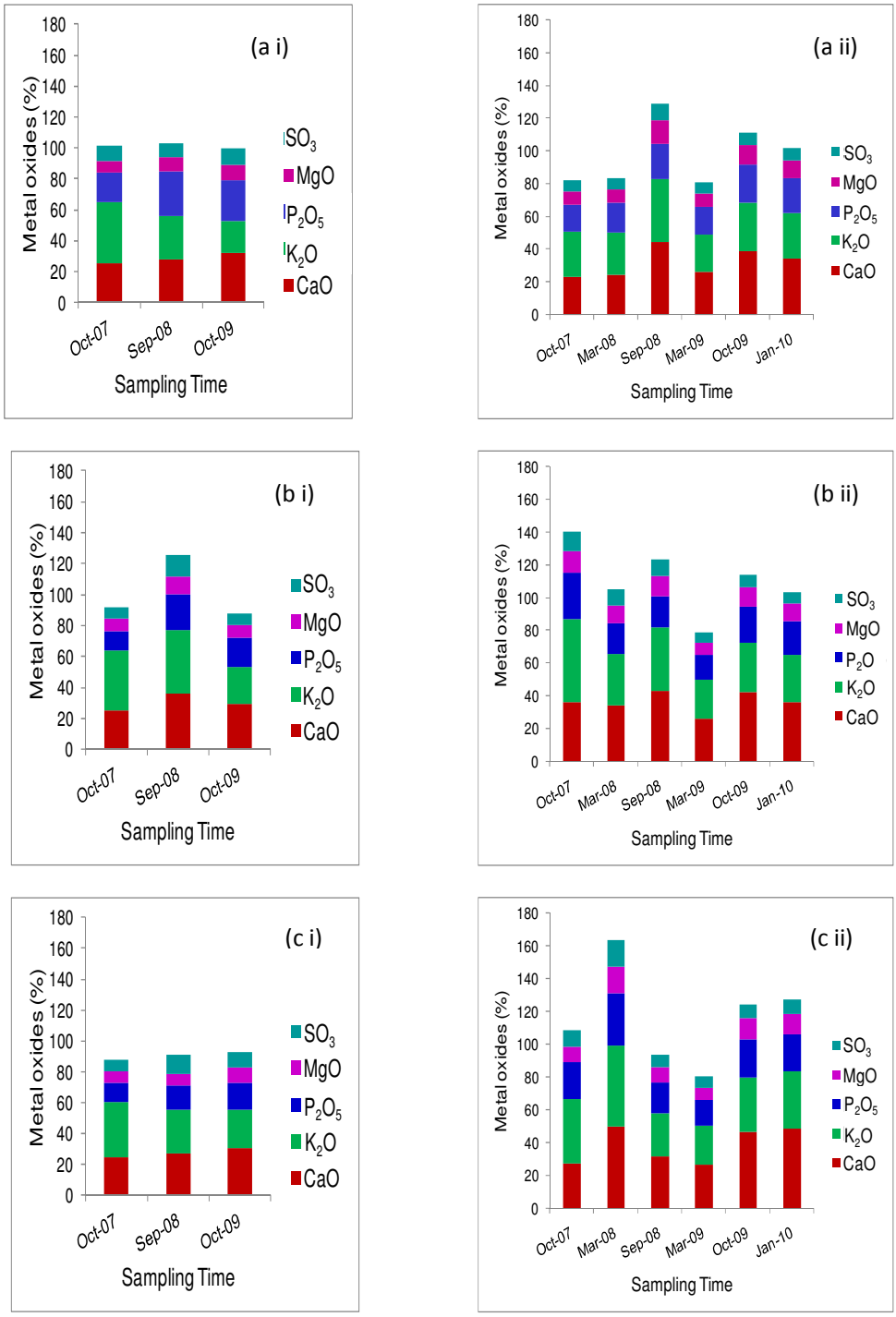


Figure 5 11 Treatment means with sampling time of major metal oxides a,b and c being treatments A, D and F respectively and i and ii being leaves and stems respectively

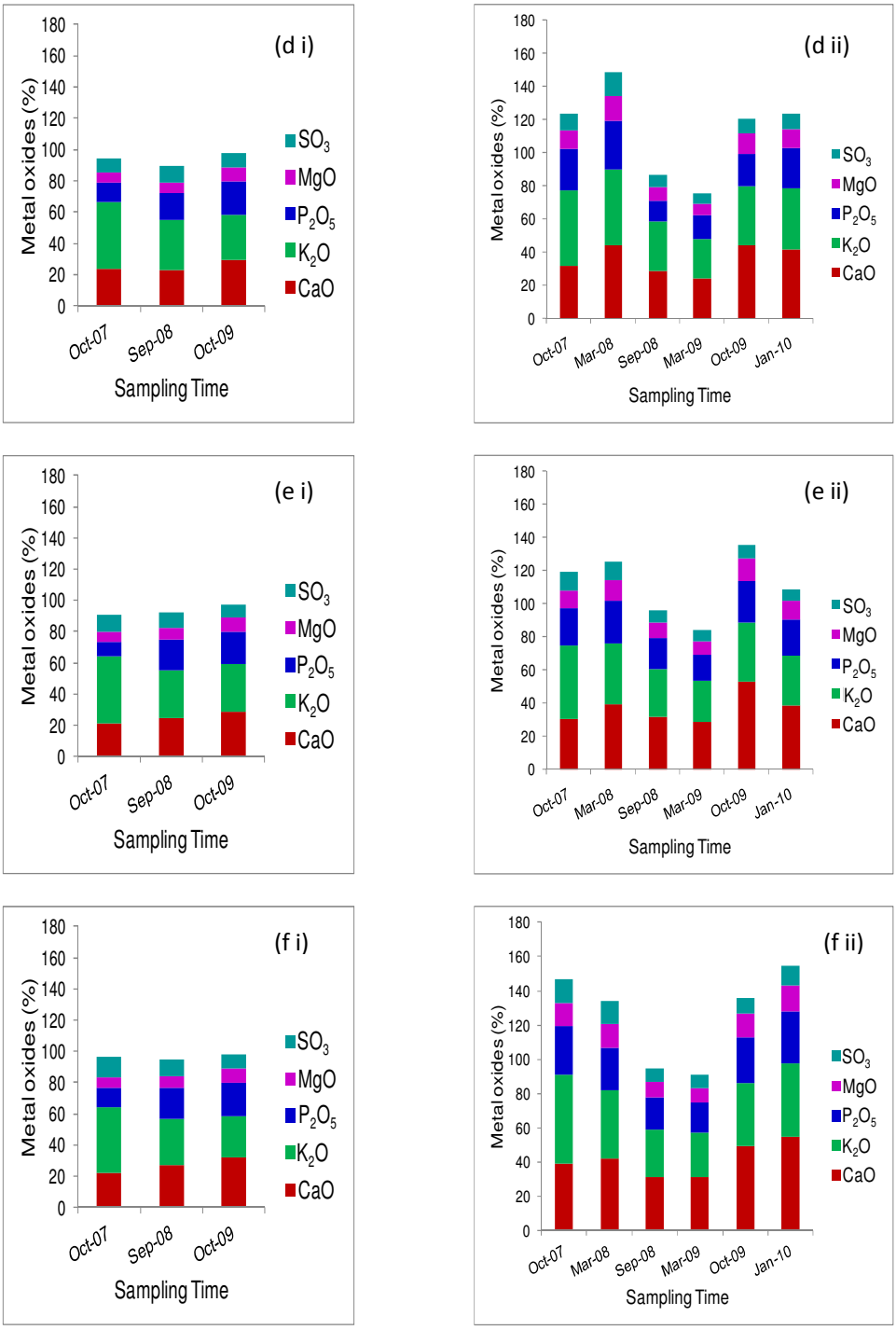


Figure 5 12 Treatment means with sampling time of major metal oxides d,e and f being treatments J, N and O respectively and i and ii being leaves and stems respectively

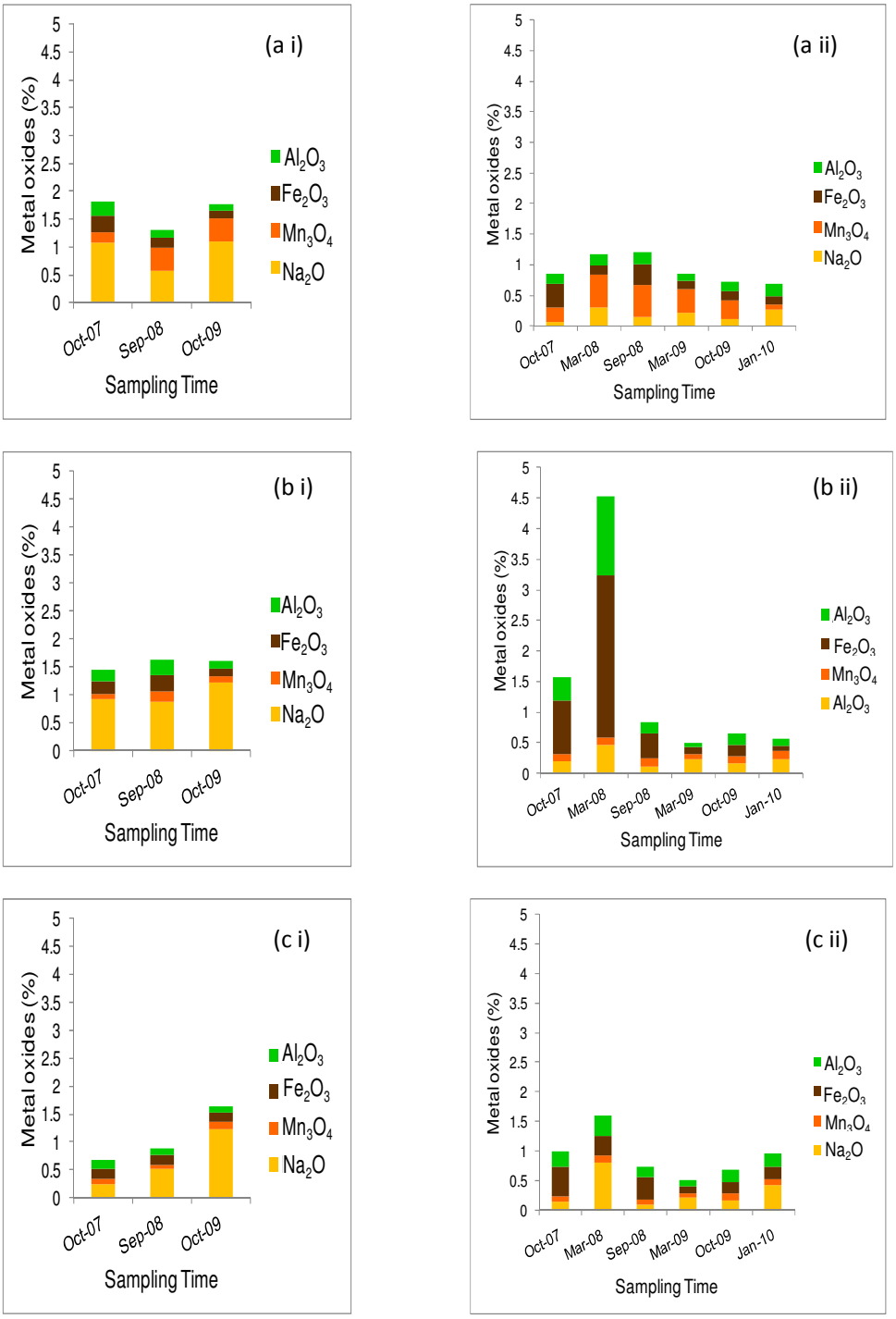


Figure 5 13 Treatment means with sampling time of minor metal oxides a,b and c being treatments A, D and F respectively and i and ii being leaves and stems respectivel

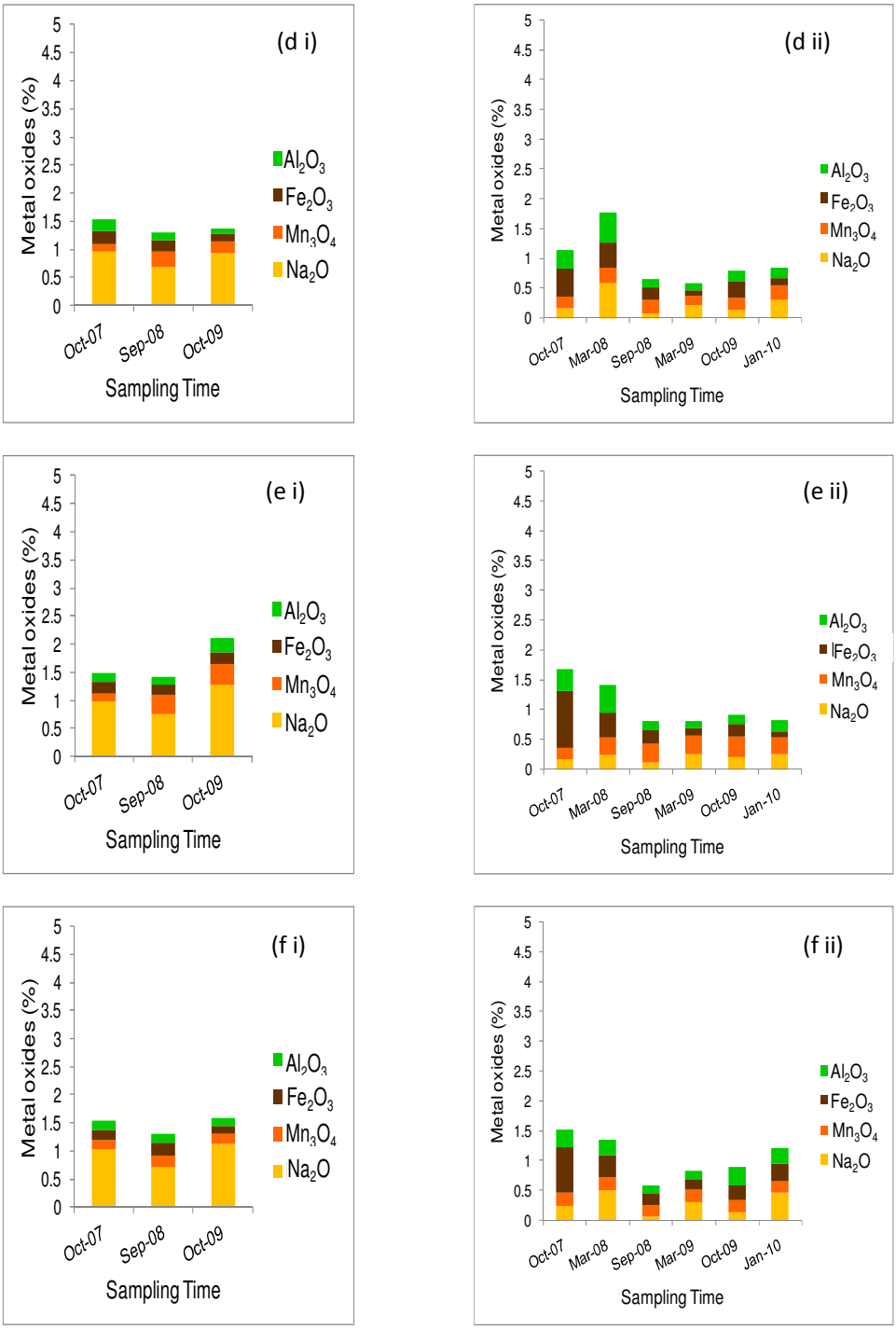


Figure 5 14 Treatment means with sampling time ofminor metal oxides d,e and f being treatments J, N and O respectively and i and ii being leaves and stems respectively

5.5.5.2 Minor Metals

The minor metals consist of Na_2O, Al_2O_3, Mn_3O_4, Fe_2O_3 and TiO_2. TiO_2 has not been included in the Figures since it is present in very minute quantities (<0.01%). Minor metals make up approximately 2.5% of the ash composition except in the case of Treatment D where they make up 4.5% of it.

Statistical analysis of the influence of treatment and sampling time has only been carried out for a few of the major components (CaO, K2O and P2O5) of the ash.

5.5.5.3 CaO (wt %)

Generally CaO in biomass ash increases the ash melting temperature making it a desirable component in power plant fuel as it helps reduce the damage occurring in furnaces and boilers due to slagging and fouling (Baxter et al., 1998).

Table 5 11 Treatment means of CaO (%) in the ash for all sampling times

Treatment	Leaves			Stems					
	Oct-07	Sep-08	Oct-09	Oct-07	Mar-08	Sep-08	Mar-09	Oct-09	Jan-10
A	25.41	27.98	32.09	23.00	24.30	44.70	26.40	39.30	34.70
D	25.04	35.70	29.51	36.60	34.80	43.00	26.60	42.80	36.10
F	24.95	26.98	30.70	27.70	49.90	31.70	26.80	46.80	48.70
J	23.63	22.74	29.58	31.60	44.20	28.90	24.50	44.40	42.10
N	21.50	24.91	28.70	30.80	39.60	31.70	29.00	52.90	38.80
O	22.13	26.97	32.40	38.90	42.00	31.50	31.20	49.60	54.90

The wt % CaO of SRC willow ash ranges from 21-55% with stems having higher (23-55 wt % CaO) than leaves (21-36 wt % CaO). The treatment means of wt % CaO are listed in Table 5.11 and the corresponding Fprs, LSDs and SEDs are listed in Table 5.12. The results are also shown graphically in Figures 5.15 and 5.16.

Table 5 12 ANOVA parameters for treatment means of CaO (%) in the ash

		Leaves			Stems		
		SED	LSD	$Fpr_{0.05}$	SED	LSD	$Fpr_{0.06}$
N effect	Treatment	1.514	4.203	0.338	2.480	6.880	0.125
Treatments	Time	1.436	3.521	**0.013**	4.800	12.080	0.065
A, D, F	Treatment.Time	2.533	5.891	0.092	7.980	19.810	0.257
K effect	Treatment	2.828	7.851	0.331	2.190	6.080	0.196
Treatments	Time	1.292	3.108	**0.008**	5.370	13.740	0.141
A, D, J	Treatment.Time	3.366	8.242	**0.023**	8.770	22.180	0.453
S effect	Treatment	1.037	2.880	**0.019**	4.460	12.380	0.517
Treatments	Time	1.435	3.290	**0.004**	4.620	11.750	0.059
A, D,N	Treatment.Time	2.279	5.051	0.077	8.550	21.180	0.421
Sewage pellets	Treatment	1.983	4.418	0.188	3.180	7.080	0.187
effect	Time	0.983	2.136	**<0.001**	3.470	8.100	**0.002**
All treatments	Treatment.Time	2.792	8.963	0.064	8.380	19.420	0.427

5.5.5.3.1 Treatment Differences for CaO (%) in ash

Significant differences within treatments are only seen for leaves for the S effect. Here addition of S fertiliser (Treatment N) lowers the wt% CaO in the ash from resultant leaves. The % CaO increases throughout the growing period with Treatment A having a higher CaO compared to Treatment N The sample taken in Sep-08 for Treatment D has the highet wt % CaO.

5.5.5.3.2 Sampling Time Differences for CaO (%) in ash

Significant differences are seen for the leaves for all 4 effects. There is a general trend of increasing CaO with sampling time except in the case of Treatments D and J. For Treatment D, the wt % CaO increases from Oct-07 to Sep-08 and then decreases again in Oct-09 while Treatment J shows the opposite effect where the wt % CaO decreases from Oct-07 to Sep-08 and then increases in Oct-09. For the stems, there is a significant difference in sampling times for the sewage pellets effect (Figure 5.16). Treatments A, J and N behave similarly with wt % CaO increasing from autumn to spring in the 1st year while wt % CaO decreases from autumn to spring in the 2nd and 3rd years. For Treatments F and O, the wt % CaO increases from autumn to spring in the 1st and 3rd years and decreases in the 2nd year and for Treatment D, the wt % CaO decreases from autumn to spring in all 3 years.

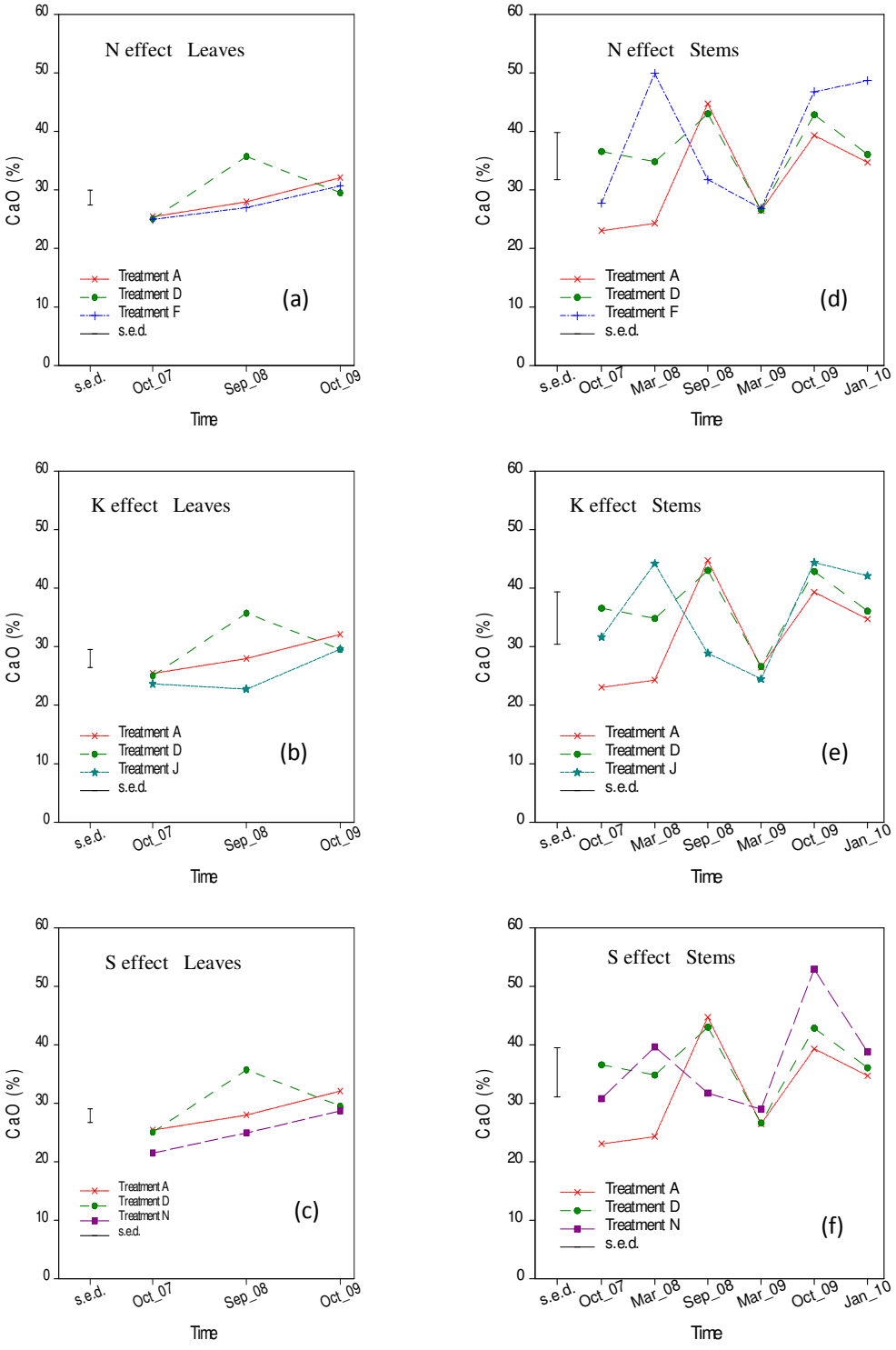


Figure 5 15 Treatment means with sampling time of CaO (%) for leaves (a-c) and stems (d-f) for the N, K and S effect respectively

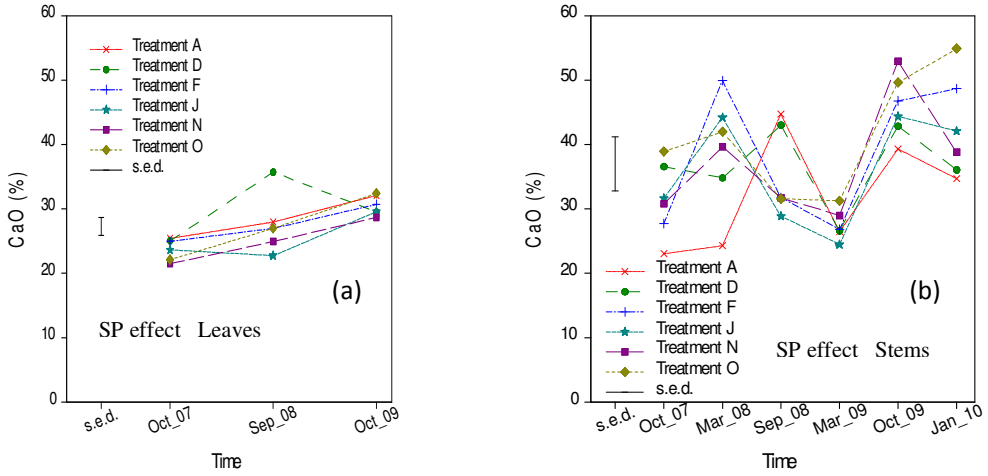


Figure 5 16 Treatment means with sampling time of CaO (%) for leaves (d) and stems (h) for the sewage pellets effect

5.5.5.3.3 Interactions for CaO (%) in ash

There is an interaction between treatment and sampling time for the leaves for the K effect. The wt % CaO generally increases over the growth period but for Treatments D and J, the samples taken in Sep-08 have the highest and lowest wt % CaO respectively

5.5.5.4 K_2O (wt %)

K_2O, when present in biomass ash, decreases the ash melting temperature causing slagging and fouling in furnaces and boilers (Jenkins et al., 1998).

Table 5 13 Treatment means of K_2O (%) in the ash for all sampling times

Treatment	Leaves			Stems					
	Oct-07	Sep-08	Oct-09	Oct-07	Mar-08	Sep-08	Mar-09	Oct-09	Jan-10
A	39.54	27.84	20.57	28.02	25.95	38.27	22.48	29.33	27.48
D	39.20	40.99	24.06	50.34	31.04	39.22	23.61	30.21	28.98
F	35.24	28.30	25.08	39.80	49.17	26.41	24.13	33.38	34.98
J	42.43	32.32	28.32	46.03	46.03	29.71	23.50	35.91	36.34
N	42.71	30.30	30.72	44.28	36.82	29.10	24.50	35.98	30.20
O	42.27	29.88	26.01	52.00	39.90	27.42	26.25	36.92	42.95

Table 13 shows the treatment means of wt % K_2O in the ash for stems and leaves. Stems (23-52 wt %) have higher wt % K_2O compared to leaves (24-43 wt %). Table 5.8b tabulates some of the statistical parameters for wt % K_2O and the data is shown graphically in Figures 5.17 and 5.18.

Table 5 14 ANOVA parameters for treatment means of K_2O (%) in the ash

		Leaves			Stems		
		SED	LSD	$Fpr_{0.05}$	SED	LSD	$Fpr_{0.06}$
N effect	Treatment	1.347	3.741	**0.026**	4.190	11.640	0.382
Treatments	Time	1.761	4.398	**<0.001**	4.610	11.490	0.105
A, D, F	Treatment.Time	2.832	6.722	0.058	8.410	20.490	0.209
K effect	Treatment	2.327	6.462	0.138	4.050	11.250	0.267
Treatments	Time	1.632	4.026	**<0.001**	4.560	11.170	0.061
A, D, J	Treatment.Time	3.277	7.742	**0.048**	8.280	19.850	0.290
S effect	Treatment	1.681	4.668	0.052	3.830	10.650	0.395
Treatments	Time	1.817	4.321	**<0.001**	4.180	10.150	0.043
A, D, N	Treatment.Time	3.071	6.982	**0.027**	7.640	18.200	0.359
Sewage pellets	Treatment	2.276	5.071	0.107	3.486	7.768	0.254
effect	Time	1.246	2.708	**<0.001**	2.964	6.830	**<0.001**
All treatments	Treatment.Time	3.375	7.193	**0.036**	7.490	17.098	0.269

5.5.5.4.1 Treatment Differences for K_2O (%) in ash

There is a significant treatment difference in wt % K_2O for leaves for the N effect. Treatment D has the highest wt % K_2O with the sample taken in Sep-08 having the highest wt % K_2O overall.

5.5.5.4.2 Sampling Time Differences for K_2O (%) in ash

All 4 treatment effects show a significant difference with sampling time for leaves. There is a general trend of wt % K_2O decreasing over the growth period except in the case of Treatments D and N. For treatment D, wt % K_2O increases from Oct-07 to Sep-08 and then decreases from Sep-08 to Oct-09 and for Treatment N it decreases from Oct-07 to Sep-08 and then remains stable. A significant difference in wt % K_2O is also seen in the stems for the sewage pellets effect. The wt % K_2O decreases from autumn to spring for all 3 years for Treatments A, D and N while it increases in the 1st and 3rd years and decreases in the 2nd year from autumn to spring for Treatment F. For Treatment J,

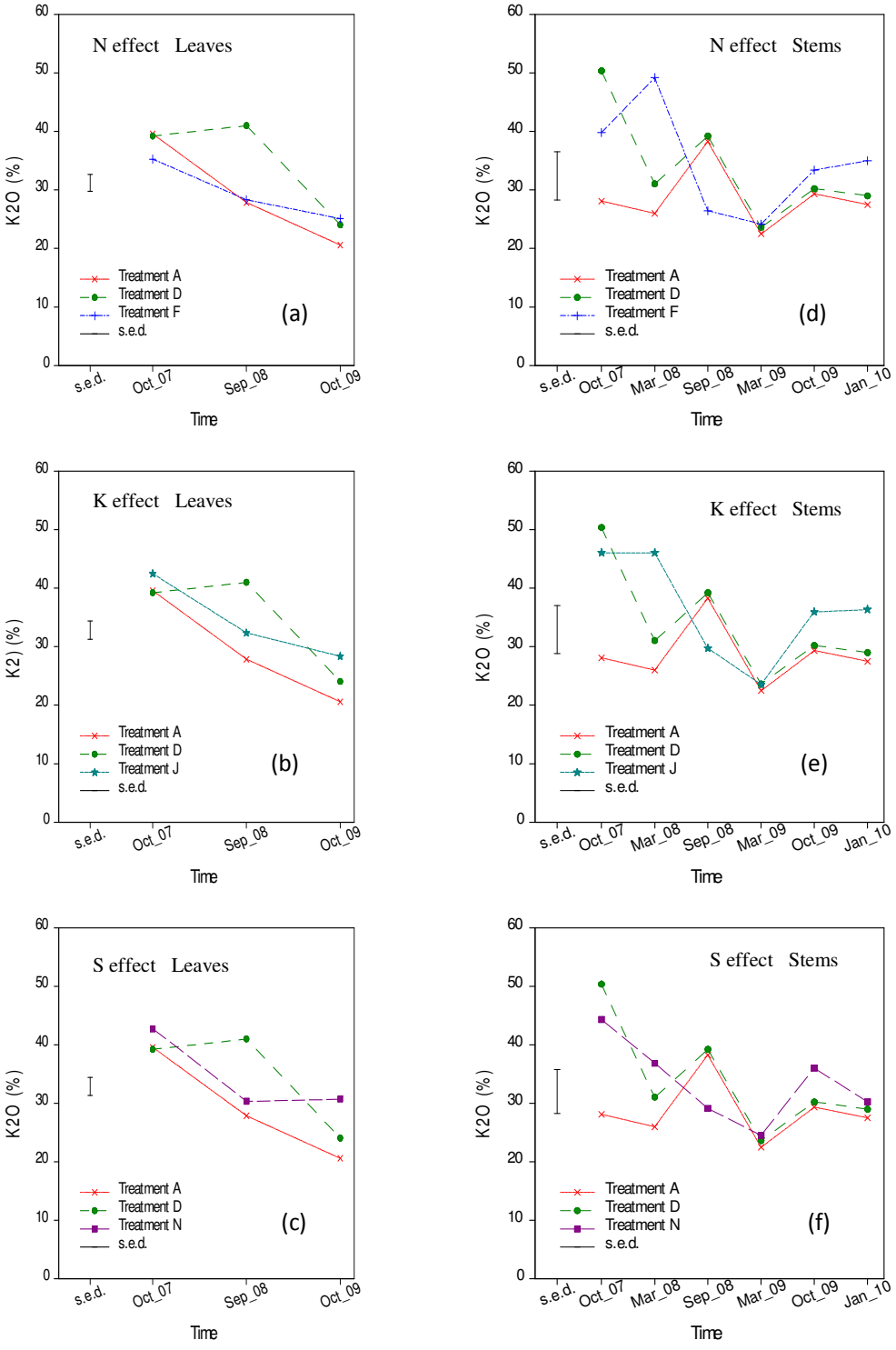


Figure 5 17 Treatment means with sampling time of K_2O (%) for leaves (a-c) and stems (d-f) for the N, K and S effect respectively

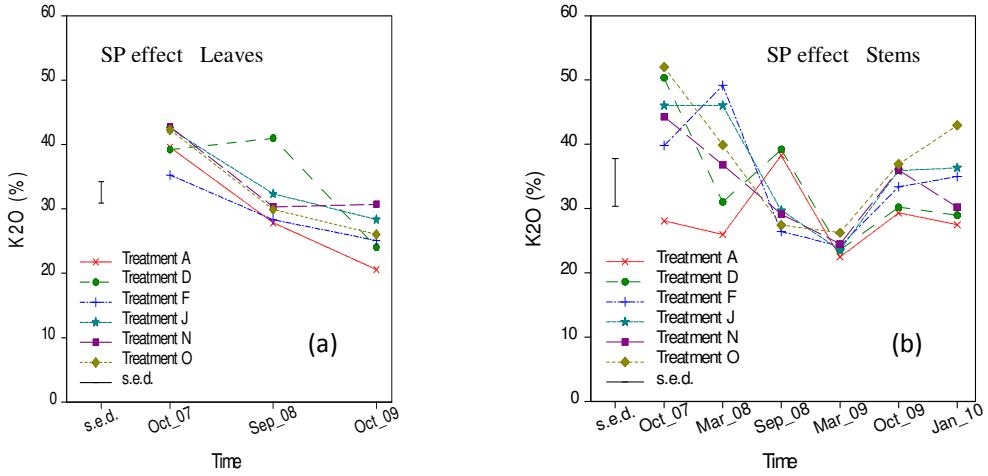


Figure 5 18 Treatment means with sampling time of K_2O (%) for leaves (a) and stems (b) for the sewage pellets effect

it remains stable in the 1st year, then decreases in the 2nd year and increases in the 3rd year and for Treatment O it decreases in the first 2 years and then increases in the 3rd year.

5.5.5.4.3 Interactions for K_2O (%) in ash

Significant differences are seen for leaves for the K, S and sewage pellets effects. For the K and S effects, Treatments J and N respectively have the highest wt % K_2O except in the case of the Sep-08 sample for which Treatment D has the highest wt % K_2O. The same applies for the sewage pellets treatment with Treatments J and N having the higher wt % K_2O.

5.5.5.5 P_2O_5 (wt %)

P_2O_5 also decreases the ash melting temperature and hence its presence is very undesirable in biomass used in power plants (Vassilev et al., 2010). The ashes of SRC willow contain high amounts of P_2O_5.

Table 5 15 Treatment means of P_2O_5 (%) in the ash for all sampling times

Treatment	Leaves			Stems					
	Oct-07	Sep-08	Oct-09	Oct-07	Mar-08	Sep-08	Mar-09	Oct-09	Jan-10
A	18.85	29.38	26.29	16.50	18.04	21.57	16.97	22.99	21.58
D	12.25	23.57	18.40	28.45	18.94	18.93	14.79	21.73	20.81
F	12.24	15.56	17.38	22.51	32.33	18.70	15.05	22.90	22.78
J	12.36	16.93	22.00	24.73	29.25	12.63	14.26	19.00	24.45
N	9.46	19.41	20.78	22.66	25.61	18.80	15.70	24.58	21.65
O	12.46	19.66	21.57	28.37	24.92	18.95	17.14	26.11	30.30

Generally, the stems of SRC willow have higher (14-33 wt %) P_2O_5 compared to leaves (9-30 wt %) as shown in Table 5.15. The statistical parameters to determine significant differences between treatments, sampling times and teir interaction are listed in Table 5.16 and results are shown graphically in Figures 5.19 and 5..20.

Table 5 16 ANOVA parameters for treatment means of P_2O_5 (%) in the ash

		Leaves			Stems		
		SED	LSD	$Fpr_{0.05}$	SED	LSD	$Fpr_{0.06}$
N effect	Treatment	0.786	2.182	**<0.001**	2.516	6.984	0.581
Treatments	Time	1.138	2.608	**<0.001**	2.956	7.637	0.213
A, D, F	Treatment.Time	1.791	3.972	0.086	5.308	13.322	0.298
K effect	Treatment	2.528	7.018	0.070	2.109	5.855	0.850
Treatments	Time	1.362	2.976	**<0.001**	3.125	8.094	0.198
A, D, J	Treatment.Time	3.178	7.204	0.079	5.373	13.586	0.297
S effect	Treatment	2.446	6.790	0.055	2.374	6.591	0.745
Treatments	Time	1.433	3.125	**<0.001**	2.720	6.833	0.206
A, D, N	Treatment.Time	3.176	7.098	0.435	4.912	12.047	0.459
Sewage pellets	Treatment	2.167	4.829	**0.015**	4.495	2.018	0.325
effect	Time	0.987	2.084	**<0.001**	4.827	2.052	**0.005**
All treatments	Treatment.Time	2.931	6.139	0.141	11.685	5.011	0.465

5.5.5.5.1 Treatment Differences for P_2O_5 (%) in ash

Significant differences are seen between treatments for leaves when considering the effect of N and sewage pellets on % P_2O_5 in the ash. There is a general increase in wt% P_2O_5 in the ash from Oct-07 to Oct-09 for all the treatments with the Sep-08 samples for Treatments A and D having higher wt % P_2O_5 Treatment A has the highest wt % P_2O_5. For the sewage pellets effect, all the treatments show an increasing trend in wt % P_2O_5. Treatment A has the highest wt % P_2O_5 with the Sep-08 samples for Treatments A and D being the highest and Treatment A having the highest wt % P_2O_5

5.5.5.5.2 Sampling Time Differences for P_2O_5 (%) in ash

There are significant differences in wt% P_2O_5 in the ash between sampling times for leaves for all 4 effects. Treatments A and D show an increase in wt % P_2O_5 from Oct-07 to Oct-09 with Sep-08 having the highest wt % P_2O_5. For the N, K, and S effects, Treatments F, J and N show an increase in wt % P_2O_5 from Oct-07 to Oct-09. For the sewage pellets treatment all treatments behave similarly with increasing wt % P_2O_5 with sampling times except for Treatments A and D which behave slightly differently as mentioned earlier. A significant difference is also seen for the sewage pellets effect for the stems. Treatments A, F and N behave similarly with the wt % P_2O_5 increasing from autumn to spring for the 1st year and then decreasing in the next 2 years. For Treatment D, wt % P_2O_5 decreases from autumn to spring for all 3 years while for Treatment J it increases for all 3 years. For Treatment O, it decreases for the first 2 years and then increases for the 3rd year.

5.5.5.5.3 Interactions for P_2O_5 (%) in ash

No interactions are seen between treatments and sampling times for wt % P_2O_5.

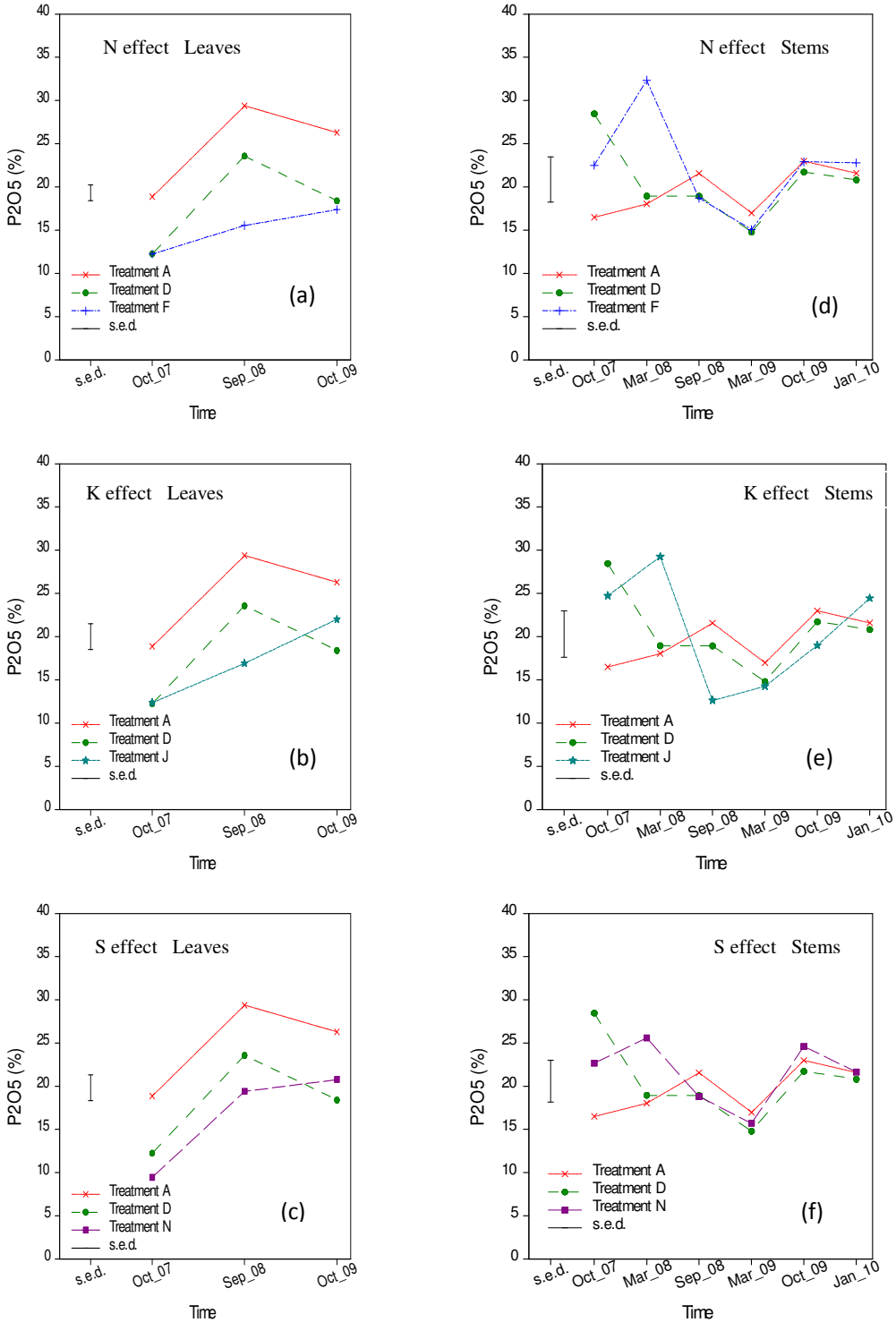


Figure 5 19 Treatment means with sampling time of P_2O_5 (%) for leaves (a-c) and stems (d-f) for the N, K and S effect respectively

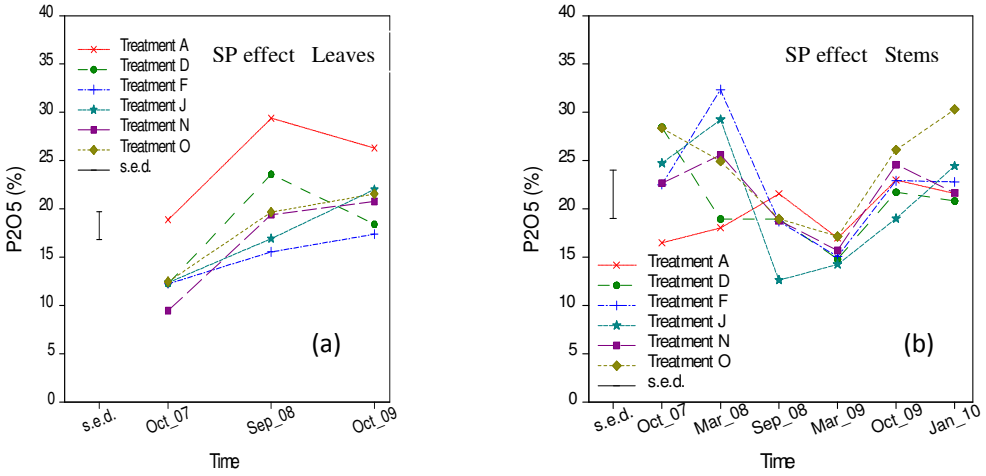


Figure 5 20 Treatment means with sampling time of P_2O_5 (%) for leaves (a) and stems (b) for the sewage pellets effect

5.5.6 Slagging and Fouling Indices

The presence of some inorganic metals such as potassium and phosphorous in the biomass ash has proven to be very problematic. For example potassium salts react with silica and sulphur to produce alkali silicates and sulphates which have very low ash melting temperatures and hence cause slagging and fouling on furnaces and boilers resulting in reduced efficiency (Jenkins et al., 1998). The presence of high amounts of phosphorous along with potassium form potassium phosphates which also have low melting temperatures and can cause slagging in furnaces (Vassilev et al., 2010). On the other hand high calcium content generally improves ash melting behaviour as it reacts with the potassium and phosphorous to produce calcium potassium phosphates which inhibit the reaction of potassium phosphate with silica thereby increasing the ash melting temperatures (Baxter et al., 1998, Lindström et al., 2007, Piotrowska P, 2009). To determine the slagging and fouling tendency of a biomass fuel, some indices like the alkali index, base to acid ratio and base percentage have been used. The alkali index and base percentages of all the individual plots for all the treatments for leaves and stems are listed in Appendix D. As before a statistical analysis is made to examine the impact of agronomy (fertilizer treatment and sampling time) on these measures of fouling and slagging.

5.5.6.1 Alkali Index

The alkali index measures the fouling tendency of a fuel It has lower and upper threshold values of 0.17 and 0.34 kg alkali/GJ respectively (Jenkins et al., 1998). It can be calculated as in Equation 4.1. Below 0.17 kg alkali/GJ, it is considered that fouling does not take place, between 0.17 and 0.34 kg alkali/GJ, fouling can probably take place and above 0.34 kg alkali/GJ fouling is virtually certain to occur.

Table 5 17 Treatment means of alkali index (% alkali/GJ) for all sampling times

Treatment	Leaves			Stems					
	Oct-07	Sep-08	Oct-09	Oct-07	Mar-08	Sep-08	Mar-09	Oct-09	Jan-10
A	1.208	1.025	0.908	0.196	0.178	0.167	0.159	0.170	0.152
D	1.283	1.497	1.078	0.225	0.175	0.159	0.160	0.160	0.151
F	1.112	1.179	0.990	0.219	0.192	0.180	0.168	0.150	0.174
J	1.330	1.155	1.141	0.228	0.201	0.204	0.182	0.178	0.155
N	1.608	1.054	1.174	0.229	0.163	0.159	0.165	0.157	0.145
O	1.535	1.228	1.066	0.205	0.176	0.167	0.182	0.154	0.171

The alkali index for leaves (0.908-1.608 kg alkali/GJ) is much higher compared to that of stems (0.145-0.229 kg alkali/GJ) as seen from the treatment means in Table 5.17. The statistical parameters for alkali index are listed in Table 5.18 for leaves and stems. Results are shown graphically in Figures 5.21 and 5.22.

Table 5 18 ANOVA parameters for treatment means of alkali index (% alkali/GJ)

		Leaves			Stems		
		SED	LSD	$Fpr_{0.05}$	SED	LSD	$Fpr_{0.06}$
N effect	Treatment	0.067	0.186	**0.048**	0.006	0.016	0.276
Treatments	Time	0.078	0.178	**0.026**	0.009	0.023	**0.003**
A, D, F	Treatment.Time	0.129	0.285	0.321	0.015	0.038	0.500
K effect	Treatment	0.088	0.245	0.118	0.004	0.012	**0.012**
Treatments	Time	0.071	0.169	**0.031**	0.009	0.022	**<0.001**
A, D, J	Treatment.Time	0.134	0.306	0.165	0.015	0.035	0.543
S effect	Treatment	0.061	0.169	**0.028**	0.006	0.016	0.935
Treatments	Time	0.086	0.192	**0.014**	0.008	0.020	**<0.001**
A, D, N	Treatment.Time	0.135	0.294	**0.047**	0.014	0.033	0.458
Sewage pellets	Treatment	0.088	0.197	0.080	0.007	0.015	0.058
effect	Time	0.065	0.136	**0.001**	0.007	0.015	**<0.001**
All treatments	Treatment.Time	0.157	0.324	0.156	0.017	0.037	0.620

5.5.6.1.1 Treatment Differences for alkali index (% alkali/GJ)

There are significant differences for leaves for the N and S effect. For the N effect, Treatment D (150 kg N/hectare) has the highest alkali index for all the sampling times while Treatment A (0 kg N/hectare) has the lowest alkali index. For the S effect, Treatment N (80 kg S/hectare) has the highest alkali index except for the Sep-08 sample; in this case Treatment D has the highest alkali index while Treatment A still has the lowest alkali index. For the stems, the K effect shows a significant difference between treatments. Treatment J (100 kg K/hectare) has the highest alkali index for all the sampling times but this is not very clear when illustrated in Figure 5.12 g since the SED is very small (SED=0.004)

5.5.6.1.2 Sampling Time Differences for alkali index (% alkali/GJ)

Significant differences in sampling time are seen for all 4 effects for both leaves and stems. The general trend for leaves for all the treatments is decreasing alkali index from Oct-07 to Oct-09 except for Treatments D, F and N. For Treatments D and F, the alkali index, increases from Oct-07 to Sep-08 and then decreases from Sep-08 and Oct-09 while for Treatment N the alkali index decreases from Oct-07 to Sep-08 and then increases from Sep-08 to Oct-09. For stems, there is a decrease in alkali index from autumn to spring for all 3 years for Treatments A, D, F and J. However for Treatment N, the alkali index decreases from autumn to spring for the 1st and 3rd years and increases in the 2nd year. For Treatment O, the alkali index decreases from autumn to spring in the 1st year and then decreases in the next two years. Overall, the alkali index decreases over the three years for both leaves and stems making the third year the optimum time to harvest the crop since it has the lowest tendency to cause fouling. The time of year to harvest the crop to obtain an optimum fuel would be autumn due to the lower alkali index at that time.

5.5.6.1.3 Interactions for alkali index (% alkali/GJ)

There is an interaction between treatment and sampling time for the leaves for the S effect. The alkali index decreases over the three years and Treatment N has the highest alkali index except for the Sep-08 sample in which case Treatment D has the highest alkali index.

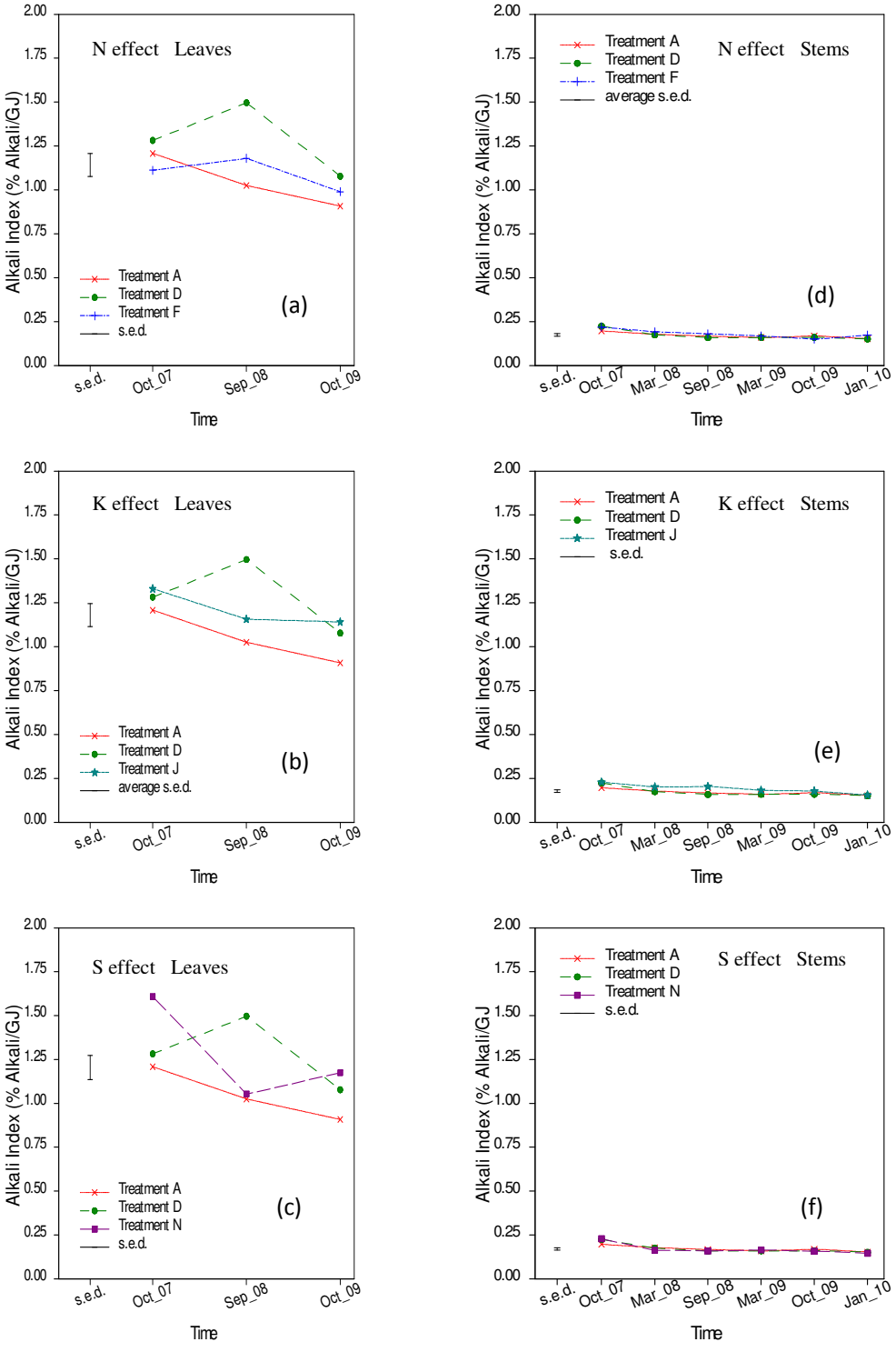


Figure 5 21 Treatment means with sampling time of alkali index (% alkali/GJ) for leaves (a-c) and stems (d-f) for the N, K and S effect respectively

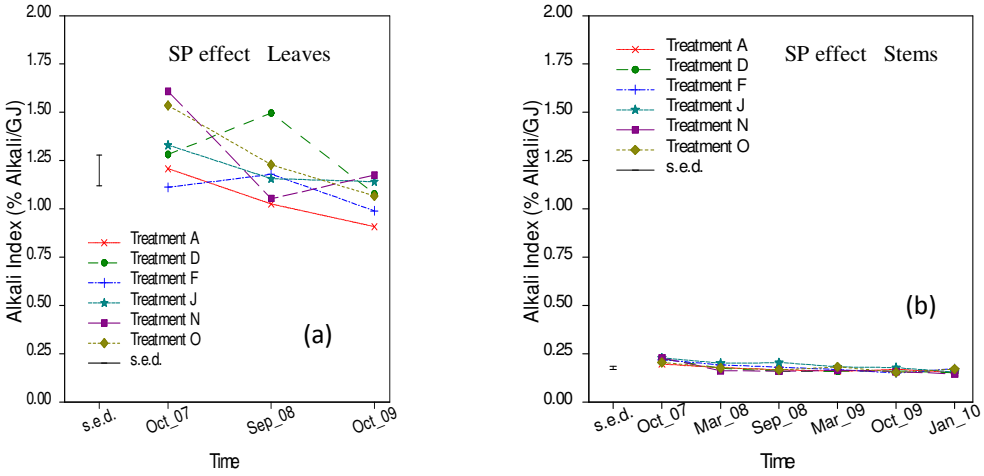


Figure 5 21 Treatment means with sampling time of alkali index (% alkali/GJ) for leaves (a) and stems (b) for the sewage pellets effect

5.5.6.2 Base Percentage

The base percentage of a fuel consists of the basic oxides, CaO, K_2O, MgO, Na_2O and Fe_2O_3. A study done by Bryers showed a parabolic relationship between ash fusion (hemisphere) temperature and the base percentage of a fuel (Bryers, 1996). Ash fusion temperatures have not been measured for the SRC willow agronomy field trial since sufficient sample was not available. However ash fusion temperatures were measured for different genotypes of SRC willow and this has been discussed in Chapter 6. For the agronomy trial we have investigated at the differences in base percentage for different treatments and for different sampling times.

Table 5 19 Treatment means base percentage for all sampling times

Treatment	Leaves			Stems					
	Oct-07	Sep-08	Oct-09	Oct-07	Mar-08	Sep-08	Mar-09	Oct-09	Jan-10
A	74.23	65.15	64.02	59.30	59.00	97.60	57.90	81.00	73.30
D	73.21	89.31	63.20	100.90	79.20	95.10	58.30	85.20	76.00
F	69.27	63.71	66.59	77.80	116.50	67.80	59.10	93.50	96.40
J	74.53	62.79	67.26	89.40	106.00	67.20	55.40	93.10	90.50
N	71.34	64.20	70.07	86.60	89.50	70.50	62.20	103.10	80.40
O	72.32	65.28	68.75	105.70	96.50	68.50	66.70	100.80	113.50

Table 5.19 lists the treatment means for base percentage for leaves and stems for all sampling times. Stems (~55-100%) have a higher base percentage compared to leaves (~62-90%) and the base percentage of stems exceeds 100% in some cases due to the overestimation of oxygen based components in the ash. Table 5.20 lists the statistical parameters for the base percentage. Figures 5.23 and 5.24 display the results in Table 5.19 in graphical form.

Table 5 20 ANOVA parameters for treatment means of base percentage

		Leaves			Stems		
		SED	LSD	$Fpr_{0.05}$	SED	LSD	$Fpr_{0.06}$
N effect	Treatment	1.643	4.562	**0.012**	7.230	20.070	0.243
Treatments	Time	1.782	4.365	**0.005**	10.760	27.140	0.184
A, D, F	Treatment.Time	3.008	6.996	**0.001**	18.480	45.690	0.235
K effect	Treatment	1.888	5.241	**0.029**	6.880	19.110	0.258
Treatments	Time	1.861	4.659	**0.006**	11.460	28.850	0.202
A, D, J	Treatment.Time	3.239	7.645	**0.002**	19.380	47.940	0.373
S effect	Treatment	0.690	1.917	**<0.001**	9.110	25.300	0.457
Treatments	Time	1.731	4.208	**0.007**	9.960	25.000	0.139
A, D, N	Treatment.Time	2.544	6.060	**<0.001**	18.190	44.580	0.393
Sewage pellets	Treatment	1.947	4.338	**0.015**	7.090	15.790	0.207
effect	Time	1.202	2.711	**0.002**	7.390	17.220	**0.008**
All treatments	Treatment.Time	3.093	6.790	**<0.001**	17.980	41.550	0.356

5.5.6.2.1 Treatment Differences for base percentage

There are significant differences in the base % in the leaves for all 4 treatment effects. For all 4 fertilizer effects the main difference lies in the Sep-08 sample (2^{nd} year crop) which have relatively high base percentage compared to all the other treatments and sampling times.

5.5.6.2.2 Sampling Time Differences for base percentage

Significant differences are seen in the base % of ash for leaves from all Treatment For Treatment A, base percentage decreases from Oct-07 to Oct-09.and for Treatment D, base percentage increases from Oct-07 to Sep-08 and then decreases from Sep-08 to Oct-09. For all the other treatments, the opposite is true with base

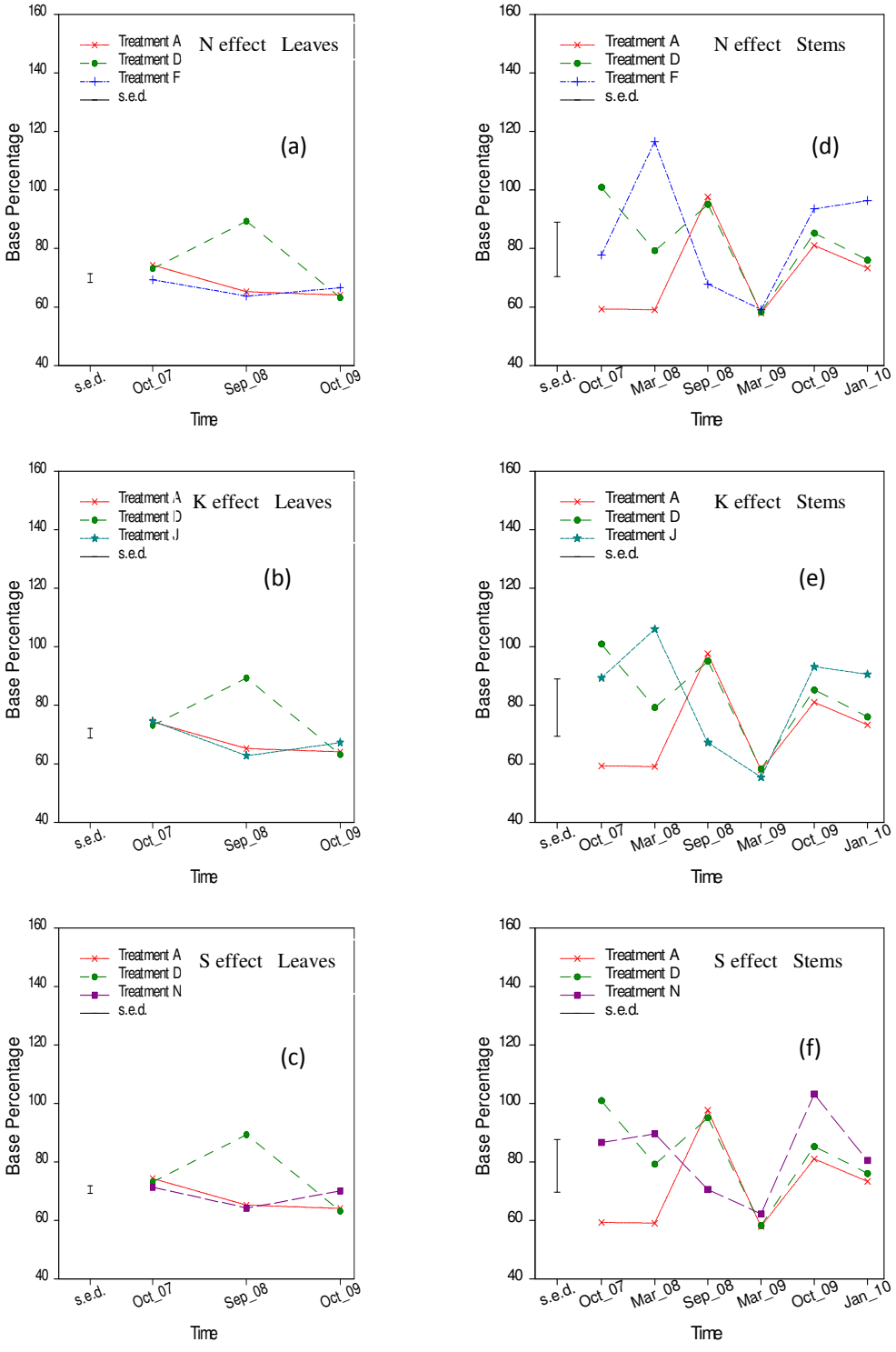


Figure 5 22 Treatment means with sampling time of base percentage for leaves (a-c) and stems (d-f) for the N, K and S effect respectively

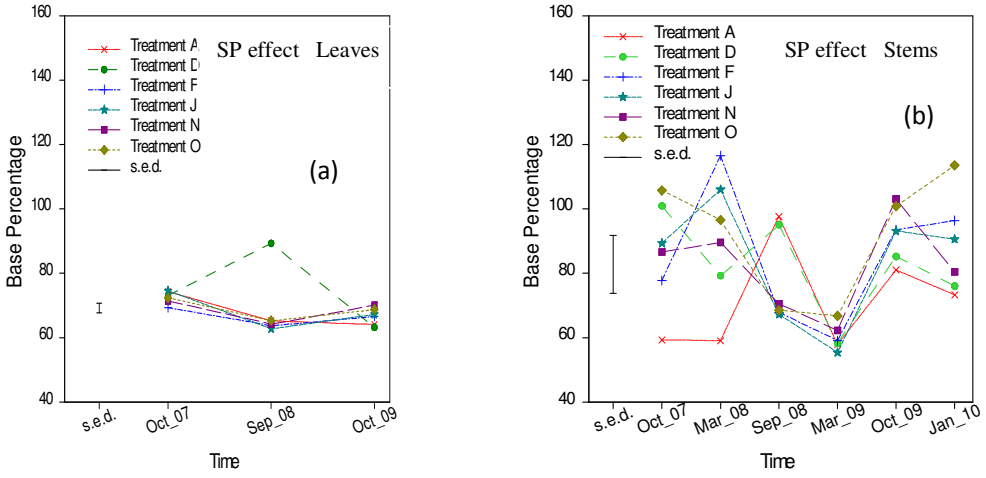


Figure 5 23 Treatment means with sampling time of base percentage for leaves (a) and stems (b) for the sewage pellets effect

percentage decreasing from Oct-07 to Sep-08 and then increasing from Sep-08 to Oct-09 . For the stems, a significant difference is seen in the base % of the ash from stems for the sewage pellets effect. For Treatments A and D, the base percentage decreases from autumn to spring for all 3 years. For Treatments J and N, base percentage increases from autumn to spring for the 1st year and then decreases for the 2nd and 3rd year. For treatment F it increases for the 1st and 3rd years and decreases for the 2nd year while for Treatment O it decreases for the 1st year and increases for the 2nd and 3rd year.

5.5.6.3 Base to Acid Ratio

The base to acid ratio ($R_{b/a}$) is a measure of the tendency of a fuel to cause slagging in furnaces in power plants and it can be calculated using Equation 4.2. Normally P_2O_5 is not included in the equation since coal has low phosphorous contents. However previous studies (Baxter et al., 2012, Lolja et al., 2002) have shown that the addition of P_2O_5 gives a better correlation due to the high phosphorous content in the biomass. The lower and upper threshold values of the base to acid ratio for coal are 0.5 and 1 respectively (IEA, 1994). Threshold values for biomass are not yet known but are assumed to be lower than that for coal.

For the SRC willow, the $R_{b/a}$ is only calculated for a sub set of the samples since silica was only analysed for those. The silica contents and $R_{b/a}$ for the sub-set of samples are listed in Table 5.12. The silica content of SRC willow is <14% The silica content for leaves for Sep-08 is higher than that of Oct-07 and hence the $R_{b/a}$s for Sep-08 are lower compared to Oct-07. For stems, the silica content is > 8% with the $R_{b/a}$ ranging between 2 and 3.

The high $R_{b/a}$s indicates that SRC willow has a high tendency for slagging.

Table 5 21 Silica contents in ash and Base to Acid ratios for leaves Oct-07 and Sep-08 and stems Mar-09

Treatment	Plot	Leaves Oct-07				Leaves Sep-08				Stems Mar-09			
		SiO_2 (%)	Base (%)	Alkali (%)	$R_{b/a}$	SiO_2 (%)	Base (%)	Alkali (%)	$R_{b/a}$	SiO_2 (%)	Base (%)	Alkali (%)	$R_{b/a}$
A	7	2.67	77.86	23.39	3.33	3.23	66.48	36.22	1.84	8.25	53.98	25.44	2.12
	21	3.53	75.03	23.19	3.24	5.64	70.18	37.04	1.89	9.36	61.51	25.59	2.40
	44	3,27	69.80	20.25	3.45	8.45	58.80	32.60	1.80	9.08	58.17	26.93	2.16
D	14	2.67	77.60	15.87	4.89	5.73	91.27	33.45	2.73	9.27	58.63	24.47	2.40
	16	4.89	73.67	21.47	3.43	3.28	95.02	25.59	3.71	8.42	55.02	22.23	2.48
	32	5.23	68.37	12.89	5.30	6.59	81.63	28.07	2.91	10.63	61.11	26.21	2.33
F	6	3.25	67.88	17.27	3.93	3.75	64.22	19.32	3.32	8.26	56.96	24.52	2.32
	26	3.73	71.80	18.02	3.98	5.24	65.61	23.78	2.76	10.72	63.17	26.34	2.40
	36	5.89	68.14	14.77	4.62	6.69	61.31	19.61	3.13	9.89	57.14	23.51	2.43
J	12	3.33	79.77	16.28	4.90	1.30	64.52	16.02	4.03	10.06	50.87	22.82	2.23
	24	3.77	72.05	16.66	4.32	3.20	64.35	22.32	2.88	8.76	59.76	23.69	2.52
	39	7.37	71.78	19.21	3.74	9.52	59.49	26.90	2.21	11.05	55.49	26.46	2.10
N	15	3.15	72.31	10.10	7.16	6.18	66.69	25.19	2.65	9.65	61.75	25.51	2.42
	20	5.05	73.86	15.95	4.63	9.82	66.71	31.72	2.10	10.82	63.49	26.66	2.38
	45	6.97	67.85	17.97	3.77	10.27	59.22	28.00	2.11	10.27	61.33	26.02	2.36
O	8	2.35	67.10	13.12	5.12	13.19	62.88	36.12	1.74	8.89	83.19	30.07	2.77
	17	3.85	73.71	18.35	4.02	2.92	68.22	20.03	3.41	9.25	62.08	24.65	2.52
	31	2.20	76.13	14.82	5.14	10.21	64.73	29.66	2.18	9.84	54.94	25.10	2.19

$R_{b/a}$ Base to Acid ratio

5.5.7 Discussion and Conclusions for Fuel Characterisation

An optimum fuel would be one with low nitrogen and sulphur contents to avoid emissions of NO_x and SO_x. It would also be one with low ash contents or non-problematic ash. The ashes of biomass are very problematic and some of its inorganic components particularly K_2O, SiO_2 and P_2O_5 can lower ash melting points and cause fouling and slagging in boilers and furnaces. The nutrients applied to the crop and its harvest time highly influence the fuel properties.

5.5.7.1 Leaves and stems:

The nitrogen and ash contents of leaves are much higher than those of stems hence they would not make a very desirable fuel for power plants. The weight % CaO in SRC willow stems (23-55%) is much higher than that of leaves (21-36%) which is desirable since wt% CaO increases the ash melting temperature. On the other hand wt % K_2O in the ash is also higher in stems (23-52%) compared to leaves 24-43%), but this causes a problem in power stations since it lowers the ash melting temperature when it reacts with silica and sulphur. P_2O_5 is also higher in stems (14-33%) compared to leaves (9-30%). Leaves (0,908-1.608 kg alkali/GJ) are more prone to cause fouling in boilers and furnaces since they have higher alkali index compared to stems 0.145-0.229 kg alkali/GJ) while, both leaves and stems show a high risk of slagging in boilers and furnaces.

5.5.7.2 Sampling Time

A general decrease in C content of SRC willow is seen over the sampling time. This in turn influences the CV which also decreases over the sampling time since it is highly dependant on the C content. The nitrogen content for SRC willow leaves generally decreases over sampling time although the Sep-08 sample in this case has the highest nitrogen content for all 4 treatment effects. The weight % CaO and wt % K_2O increase and decrease respectively in the leaves of SRC willow over the sampling time for all treatments except for Treatments D and N in the latter case. The alkali index for both the leaves and stems decreases over the 3 year growth period as well as the annual growing season. This reduces the fouling tendency of the crop

5.5.7.3 Treatment

Treatment J has high C content which could be the result of both K and N as fertilizers. Nitrogen content in the fuel is not only influenced by the addition of nitrogen fertilizer but also the addition of K and S as fertilizers since Treatments J and N have high nitrogen contents. Fertilizer treatment usually does not influence the ash content of the fuel, but the application of sewage pellets as fertilizer may result in low ash.

Some positive influences of fertilizer treatment have been identified eg the addition of both nitrogen and potassium increases the carbon content of SRC willow which in turn improves the calorific value of the fuel. However this dataset is still insufficiently small to make firm conclusions regarding the benefit of a treatment response. They also need to be considered alongside information on yield and greenhouse gas savings. SRC willow is usually harvested when the leaves have fallen. By doing so, not only are nutrients recycled to the soil from the leaf litter but, the fuel also has improved qualities which are desirable during combustion in boilers and furnaces. There have been anecdotes of farmers harvesting the green willow in order to meet demands due to its limited supply in the UK. The high ash contents would lead to higher alkali components of ash which lower ash melting temperatures hence causing slagging and fouling in furnaces and boilers.

5.6 Combustion Studies of SRC willow via TGA

Combustion studies via TGA help to investigate the different stages of combustion and also allow calculation of an apparent rate of combustion at different temperatures during combustion process. The apparent rate can be used to compare the combustion characteristics of biomass with different composition.

TGA combustion runs were conducted according to Section 3.3.9.2 with a heating rate of 25^{o}C/min from ambient temperature to 900^{o}C. The repeatability of the peak volatile combustion temperature (ie the temperature at the maximum rate of volatile combustion) is ±2.8^{o}C and that of peak char combustion temperature (ie the temperature of the maximum rate of char combustion) is ±9.6^{o}C. However char combustion peak temperature was also found to be dependant on sample weight. A sample weight of 4.5-5.5mg has been used for all the combustion tests.

5.6.1 Burning profiles from TGA combustion

Figures 5.25 and 5.26 illustrate typical mass loss and DTG curves for leaves and stems respectively. These plots are for Treatment J plot 24 of SRC willow for the different sampling times. The mass loss curve shows an initial small mass loss which is due to the evaporation of moisture, followed by a larger mass loss which is due to the release and combustion of volatile matter and char formation, followed by a mass loss due to char burnout; the residue that finally remains is the ash. The DTG is the derivative of the mass loss with time and shows two very distinct peaks. The first peak indicates the fastest rate at which volatile matter is released and combusted and the second peak indicates the fastest rate of char burnout.

The shape of the char combustion peak is often non-symmetrical when plotted against temperature because an exotherm is often seen (sample temperature increases above the furnace temperature by a few degrees and then decreases back to furnace temperature as the rate of char combustion decreases).

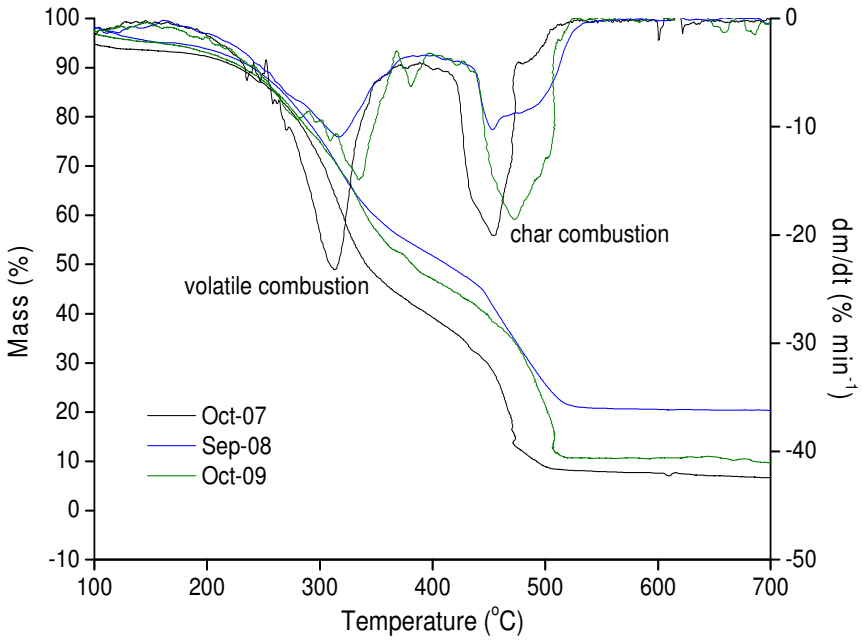


Figure 5 24 Combustion Mass loss and DTG profiles for leaves plot 24 for all sampling times

The shoulder on the volatile combustion peak indicates the combustion of hemicelluloses while the distinct peak indicates the combustion of cellulose. Lignin combusts in a wider temperature range. For stems the hemicellulose peak is not very distinct and hence the volatile combustion peak is broader for leaves compared to stems with a small shoulder on the left hand side. A small study conducted previously indicated that hemicelluloses decreases over sampling time while cellulose and lignin increase over sampling time (Gudka et al., 2010) From the DTG curves, it can be seen that the peaks have shifted over sampling time. This is due to the effect of changing concentration of some metals in the fuel and is seen in detail in Section 5.6.3.

Table 5.22 lists some of the metals and the volatile and char combustion peak temperatures for the leaves and stems for plot 24 for all sampling times. From the data in Table 5.22 we can explore how the peak temperatures shift with change in the metal contents.

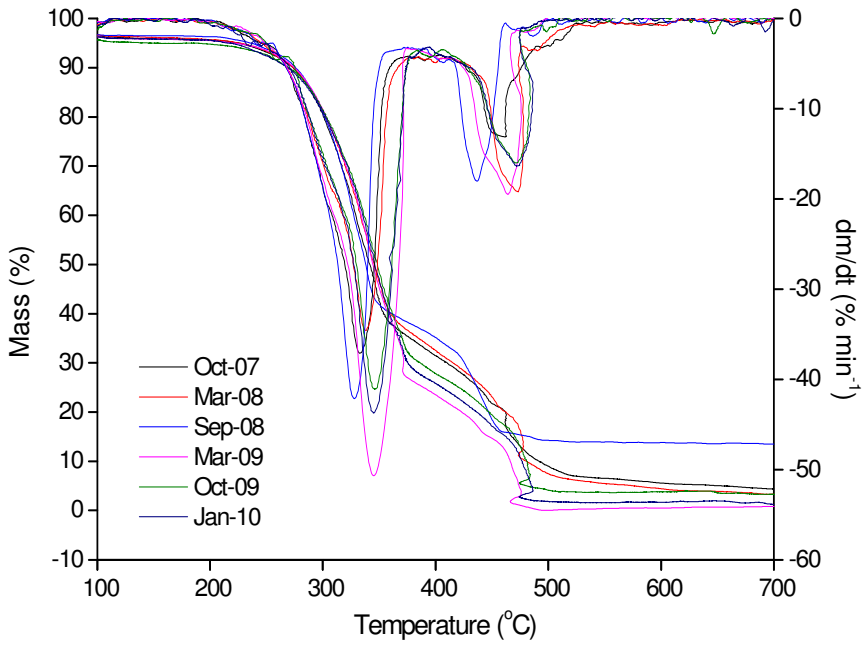


Figure 5 25 Combustion Mass loss and DTG profiles for stems plot 24 for all sampling times.

Table 5 22 Inorganic metals, and peak volatile and char combustion temperatures for leaves and stems for Plot 24 for all sampling times

Sampling Time	Fe	Ca	K	Mg	Na	P	S	Total Metals	T_{vm}	T_{char}
	mg/kg dry fuel								°C	
Leaves										
Oct-07	87.6	9440	21400	2110	355.00	3320	1890	36712.60	311	444
Sep-08	126.0	12070	19500	2870	434.00	5890	2610	40890.00	316	449
Oct-09	62.8	16000	14400	3600	463.00	6660	2900	41185.80	330	462
Stems										
Oct-07	27.9	2050	3710	582	13.60	997	388	7380.50	336	459
Mar-08	26.4	2780	3290	722	38.80	1060	489	7917.20	342	474
Sep-08	20.9	2650	2970	592	10.90	963	335	7206.80	330	459
Mar-09	12.0	2760	2950	618	37.50	921	359	7298.50	345	454
Oct-09	9.0	2900	2570	646	6.69	884	294	7015.68	350	466
Jan-10	6.8	2680	2440	605	18.60	918	318	6668.44	346	466

ANOVA has been used to look at differences between treatments and total metals for all treatments over all sampling times for the SRC willow. The effect of metals on char combustion has not been studied here since the metal contents of the

chars are not known and it would be incorrect to use the metal contents of the fuels. It is known that certain volatile metals such as K and Na are partially released during devolatilisation (Baxter et al., 1998). The peak temperatures for volatile and char combustion are listed in Appendix B for all the individual plots for all the sampling times.

5.6.2 Results and Discussion of ANOVA for combustion studies.

5.6.2.1 Volatile Combustion Peak Temperature

The volatile combustion peak temperatures for stems are higher (336-351^{o}C) than those for the leaves (308-328^{o}C) as shown in Table 5.23. The corresponding statistical parameters are listed in Table 5.24 and are presented graphically in Figures 5.27 and 5.28.

Table 5 23 Treatment means for volatile combustion peak temperature (^{o}C) for all sampling times

Treatment	Leaves (^{o}C)			Stems (^{o}C)					
	Oct-07	Sep-08	Oct-09	Oct-07	Mar-08	Sep-08	Mar-09	Oct-09	Jan-10
A	322	335	323	344	342	341	347	347	351
D	314	320	325	337	342	342	344	348	345
F	313	332	328	341	343	338	343	349	344
J	308	316	331	336	342	337	346	347	345
N	313	320	324	340	343	341	347	342	341
O	317	321	317	341	343	343	340	345	344

5.6.2.1.1 Treatment Differences for volatile combustion peak temperature (^{o}C)

There are no significant differences in volatile combustion peak temperatures for willow samples receiving different fertilizer treatments.

Table 5 24 ANOVA parameters for treatment means of volatile combustion peak temperature (^{o}C)

		Leaves			Stems		
		SED	LSD	$Fpr_{0.05}$	SED	LSD	$Fpr_{0.06}$
N effect	Treatment	3.730	10.360	0.271	1.252	3.475	0.198
Treatments	Time	3.520	9.030	0.035	1.582	3.965	**0.009**
A, D, F	Treatment.Time	6.230	14.930	0.267	2.797	6.854	0.395
K effect	Treatment	3.900	10.830	0.186	1.405	3.901	0.201
Treatments	Time	3.290	8.600	0.038	1.570	3.958	**0.004**
A, D, J	Treatment.Time	6.070	14.750	0.094	2.853	7.015	0.380
S effect	Treatment	4.750	13.200	0.294	1.224	3.397	0.131
Treatments	Time	3.540	9.090	0.102	1.792	4.523	0.066
A, D, N	Treatment.Time	6.910	16.640	0.320	3.087	7.630	0.294
Sewage pellets	Treatment	4.104	9.144	0.265	1.408	3.138	0.326
effect	Time	2.157	4.672	**<0.001**	1.370	2.996	**<0.001**
All treatments	Treatment.Time	5.954	12.668	**0.050**	3.372	7.330	0.470

5.6.2.1.2 Sampling Time Differences for volatile combustion peak temperature (^{o}C)

Significant differences in volatile combustion peak temperatures are seen for leaves from treatment of sewage pellets when sampling time is examined. There is generally an increase in volatile peak temperature over sampling time. Treatments D, J and N show an increase in volatile peak temperature from Oct-07 to Oct-09 while Treatments A, F and O show an increase from Oct-07 to Sep-08 and then a decrease from Sep-08 and Oct-09. For the stems, significant differences with sampling time are seen for the N, K and sewage pellets effect. Treatments D, F, J and N show an increase in volatile combustion peak temperature from autumn to spring for the 1st 2 years and then show a decrease for the 3rd year. Treatment A shows a decrease in the 1st year and an increase in the next 2 years while Treatment O shows an increase in the 1st year and a decrease in the next 2 years.

5.6.2.1.1 Interactions for volatile combustion peak temperature (^{o}C)

An interaction between fertilizer treatment and sampling time is seen for the leaves for the sewage pellet treatment. All treatments show a general increase in volatile peak temperature from Oct-07 to Oct-09 except Treatments A and O which show an increase from Oct-07 to Sep-08 and then a decrease from Sep-08 to Mar-09.

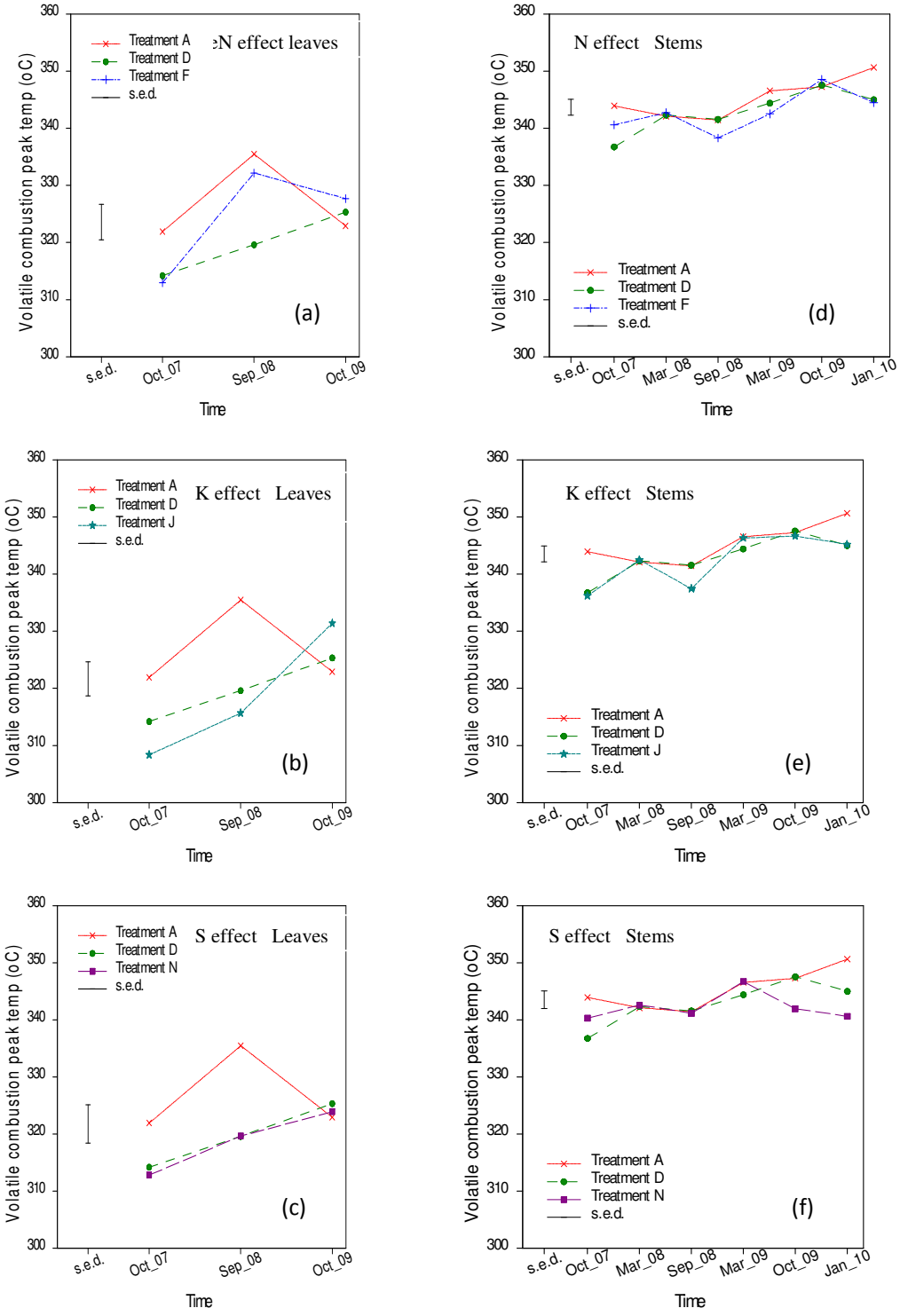


Figure 5 26 Treatment means with sampling time of volatile combustion peak temperature (^{o}C) for leaves (a-c) and stems (d-f) for the N, K and S effect respectively

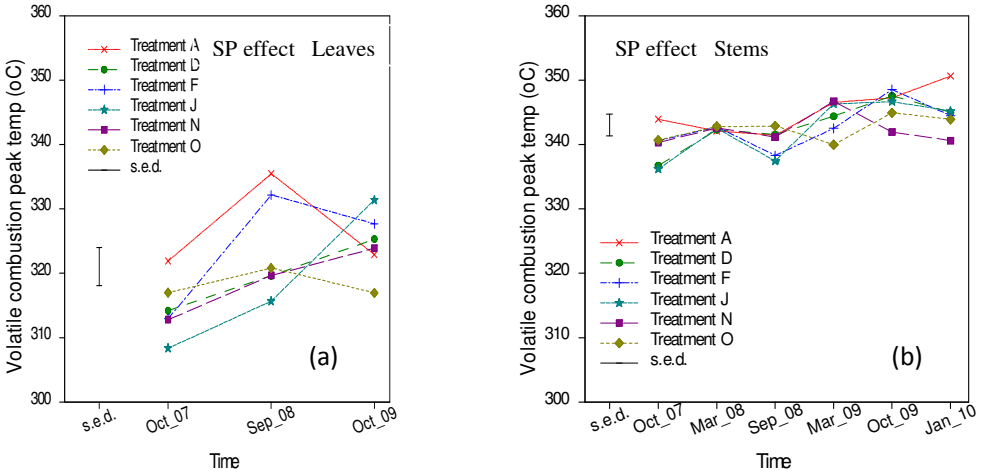


Figure 5 27 Treatment means with sampling time of volatile combustion peak temperature (^{o}C) for leaves (a) and stems (b) for the sewage pellets effect

5.6.2.2 Total Metals

The ANOVA statistical method was also applied to look at trends in total metals. The major metals include Fe, Ca, Mg, Na, K and P. Leaves have higher total metal content compared to stems (the total metal content of leaves being approximately 3 to 5 times greater than that of stems). The treatment means and statistical parameters are listed in tables 5.25 and 5.26 respectively and results are displayed graphically in Figures 5.29 and 5.30.

Table 5 25 Treatment means total metal content (mg/kg) for all sampling times

Treatment	Leaves			Stems					
	Oct-07	Sep-08	Oct-09	Oct-07	Mar-08	Sep-08	Mar-09	Oct-09	Jan-10
A	37807	43801	45343	7088	7090	7003	6743	7253	6426
D	38935	40369	42663	7407	7572	6473	6442	6854	6049
F	34598	43173	40336	7218	7313	7546	6744	6521	7297
J	36495	39012	44885	7122	7138	7125	6694	7186	6280
N	39242	38221	44105	7631	7219	6353	6831	6786	5946
O	37959	42248	42686	7843	6042	6371	7190	6278	6792

Table 5 26 ANOVA parameters for treatment means of total metal content (mg/kg)

		Leaves			Stems		
		SED	LSD	$Fpr_{0.05}$	SED	LSD	$Fpr_{0.06}$
N effect	Treatment	1638.70	4549.60	0.304	183.20	508.60	0.343
	Time	1647.70	4007.30	**0.021**	375.40	857.60	0.308
	Treatment.Time	2848.70	6585.60	0.433	621.20	1407.30	0.607
K effect	Treatment	1733.50	4812.90	0.487	133.60	371.00	0.577
	Time	1076.40	2723.60	**0.003**	363.80	856.60	0.126
	Treatment.Time	2307.00	5582.80	0.262	590.60	1381.70	0.907
S effect	Treatment	1270.10	3526.20	0.381	114.50	317.80	0.457
	Time	914.70	2086.80	**<0.001**	340.30	803.50	**0.042**
	Treatment.Time	1812.80	4065.90	0.083	550.10	1291.80	0.807
Sewage pellets effect	Treatment	1401.80	3123.40	0.476	187.70	418.10	0.476
	Time	1197.20	2626.00	**<0.001**	254.00	537.70	**0.048**
	Treatment.Time	2774.60	5958.20	0.460	598.20	1261.60	0.772

5.6.2.2.1 Sampling Time Differences for total metal content (mg/kg)

For leaves**,** significant differences between sampling times are seen for all 4 effects for the total metals as illustrated in Figures 5.29 and 5.30. There is a general increase in metal content with sampling time but with some fluctuations. For Treatments A, D, J and O, the total metals content increases from Oct-07 to Oct-09. For Treatment F, the total metal content increases from Oct-07 to Sep-08 and then decreases from Sep-08 to Oct-09. For Treatment N, total metal content decreases from Oct-07 to Sep-08 and then increases from Sep-08 to Oct-09.

For the stems, significant differences are seen for the S and sewage pellets effect. For Treatments A, D and J, total metals increase from autumn to spring in the 1st year and then decrease in the 2nd and 3rd year. For Treatment F, they increase in the 1st and 3rd years and decrease in the 2nd year. For Treatment N, they decrease in the 1st and 3rd years and increase in the 2nd year. For Treatment O, it decreases in the 1st year and increases in the next 2 years.

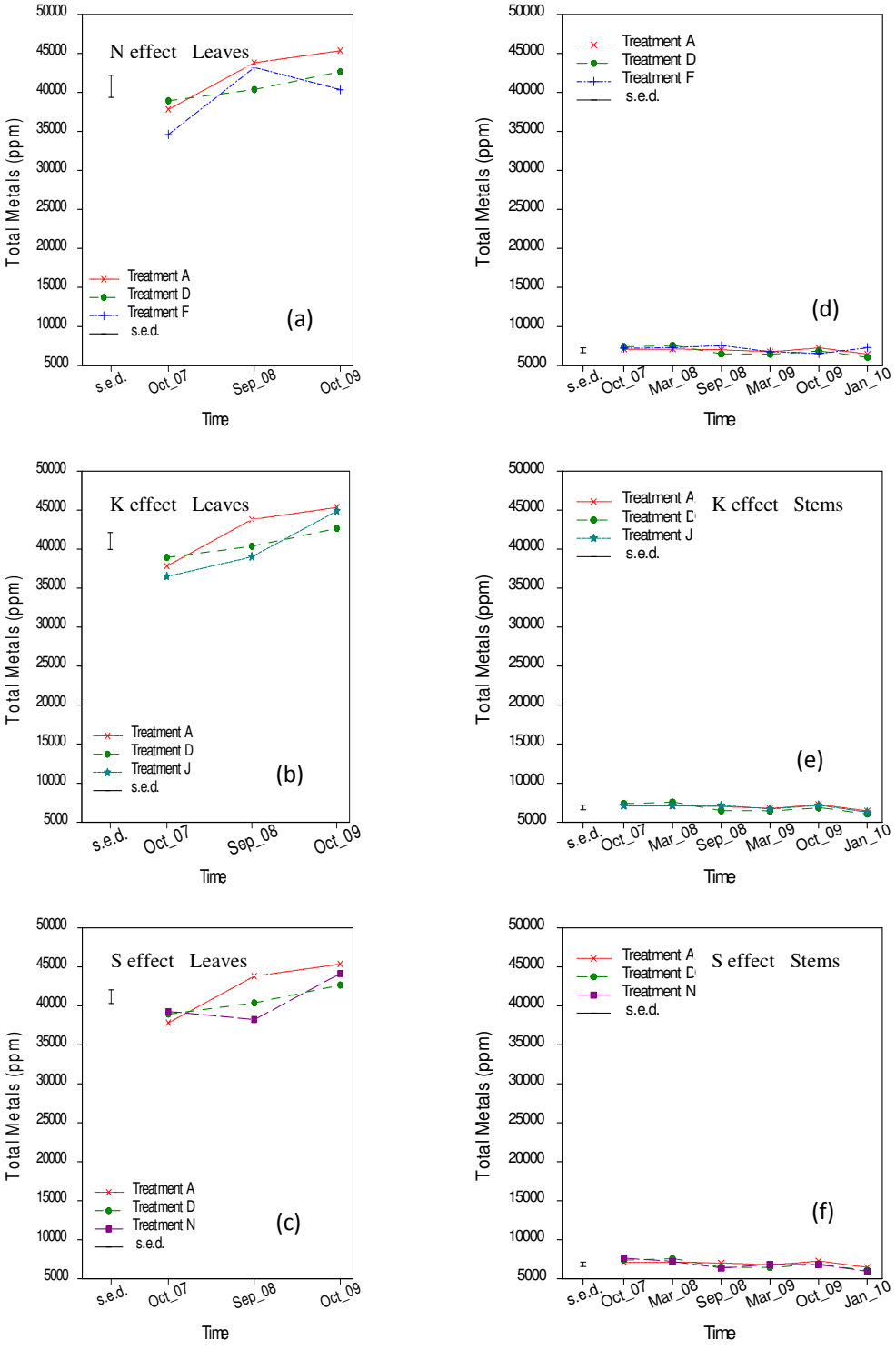


Figure 5 28 Treatment means with sampling time of total major metals (ppm) for leaves (a-c) and stems (d-f) for the N, K and S effect respectively

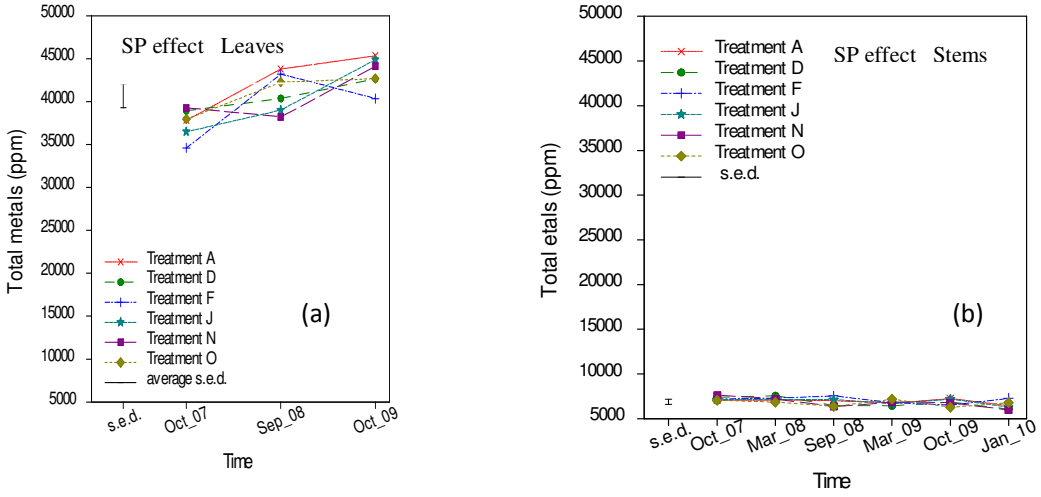


Figure 5 29 Treatment means with sampling time of total major metals (ppm) for leaves (a) and stems (b) for the sewage pellets effect

5.6.3 Influence of Inorganic Metals on Combustion

From the ANOVA analysis in Section 5.6.2, it is seen that the volatile combustion peak temperature generally increases over the 3 years for both leaves and stems. The total metals increase for leaves over the 3 years but decrease for stems. This could be due to the different cell wall composition of leaves and stems. It has been seen in previous studies that as lignin content increases, the metal content decreases for some energy crops (Fahmi et al., 2007a).

Studies done previously on SRC willow and other types of biomass have shown that some inorganic metals catalyse the combustion reaction and hence we see a shift to lower temperature in peak volatile and char combustion temperatures (Darvell L.I, 2008, Fuentes et al., 2008). Previous work on the effect of K, P, Ca, Mg and Fe on volatile and char combustion rates of SRC willow concluded that the order of rate of volatiles release and combustion was P>K>Fe>raw>demineralised>Mg>Ca and that for char combustion was K>Fe>raw>Ca-Mg>demineralised>P. Hence, P and K catalyse the volatile combustion reaction while K catalyses volatile combustion but inhibits char combustion (Fuentes et al., 2008). A similar study examined the effect of K on volatile and char combustion peak temperatures for reed canary grass and switch grass. It was found that K catalysed the volatile combustion reaction but no obvious catalytic reaction was seen for char combustion (Darvell L.I, 2008) . In these

previous studies the biomass was impregnated with known amounts of the different metals into the demineralised samples. In the current work, the inherent metals are under examination – a more difficult task since:

a) Weight %s of each individual metal are lower than in the previous studies on impregnated biomass, and
b) All inherent metals are present simultaneously which makes it difficult to separate the relative influence on combustion of the different metal species. Nevertheless, Correlation Regression Analysis have been explored as a means of examining trends for the impact of metal content (and therefore agronomy) on combustion characteristics.

5.6.4 Regression Analysis

In order to investigate the relationship between some inorganic metals and volatile combustion peak temperatures, two statistical tools; *Correlation* and *Regression* can be used.

5.6.4.1 Correlation

Correlation is the measure of the strength and direction of the linear relation between two variables. The basic assumption for correlation analysis is the Pearson's product-moment correlation co-efficient (r) which is the ratio of the population means to the standard deviation of each variable. The value of r lies between -1 and +1. If the value of r is 1, then the two variables are perfectly correlated and this concept is known as colinearity. Figure 5.31 illustrates different cases of correlation.

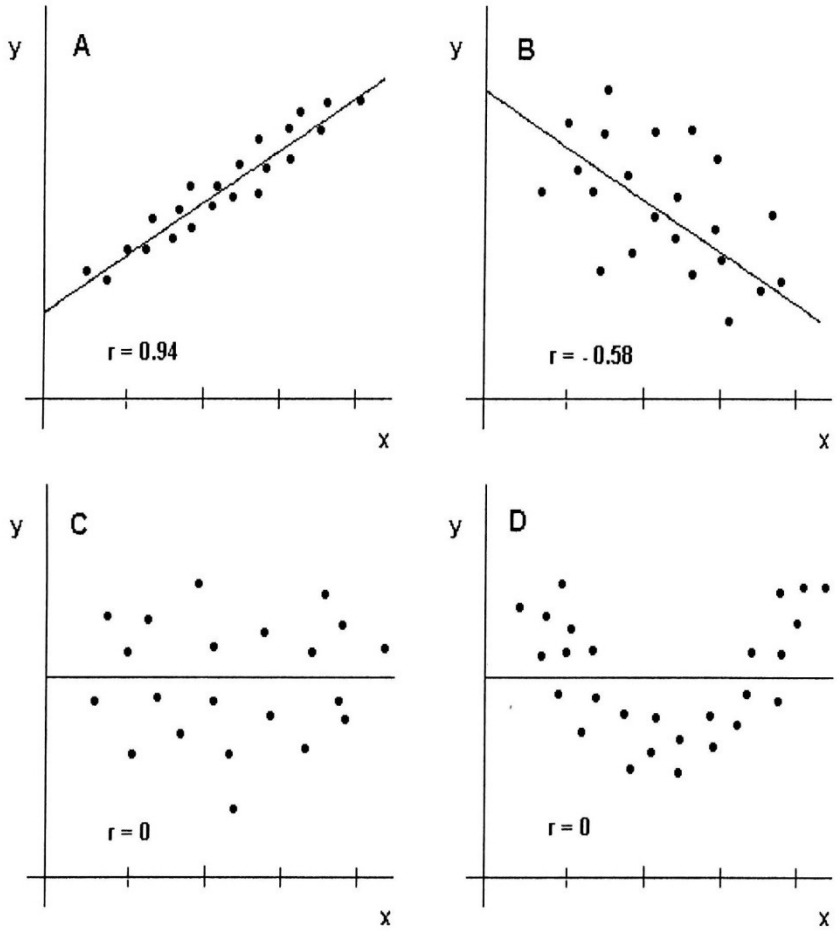


Figure 5 30 Different cases of correlation

Plot A shows a strong positive correlation (r = 0.94) while Plot B shows a weak negative correlation (r =-0.58) between x and y. Plots C and D show no linear correlation between x and y but Plot D shows some sort of relationship between x and y.

5.6.4.2 Regression

Regression methods provide us with a way of relating the value of a response/dependant (y) variable to that of a predictor/independant (x) variable using mathematical techniques. Many different mathematical models are available in regression to solve scientific problems about relationships between variables of interest. The simplest form of regression is the simple linear also known as straight line regression.

5.6.4.2.1 Simple Linear Regression

A simple linear relationship between two variables x and y can be represented as in Equation 5.5

$$y_i = \boldsymbol{\alpha} + \boldsymbol{\beta} x_i + \boldsymbol{\varepsilon}_i \qquad \text{Equation 5.5}$$

where y_i and x_i are the response and predictor variables respectively of the ith unit,$\boldsymbol{\varepsilon}$ is the point at which the line intercepts at the y axis, β is the slope of the line and $\boldsymbol{\varepsilon}_I$ is the deviation from the average response.

The quality of the goodness of a fitted line can be determined by the co-efficient of determination (r^2). For simple linear regression, r^2 is equal to the square of the Pearson's product- moment correlation co-efficient and has a value between 0 and 1. The model has a better fit with a high r^2 value which is closer to 1. For the SRC willow data, simple linear regression with groups has been used.

5.6.4.2.2 Simple Linear Regression with groups

Simple linear regression with groups helps to distinguish between different treatments exhibiting different patterns of response**s.** Each group can have its individual intercept and slope hence enabling us to make comparisons. Simple linear regression with groups can have 3 different models which can be considered when exhibiting the data and these are explained with decreasing order of complexity.

- **Separate lines model:** This model incorporates individual intercepts and slopes for each group and is illustrated in Figure 5.32a
- **Parallel lines model:** A common slope for all the groups but each group has its individual intercept represented in this model as illustrated in Figure 5.32b.
- **Single line model:** As illustrated in Figure 5.32c, this is the simplest model which incorporates a common slope and intercept for all the groups and is equivalent to fitting a single model to the complete data set.

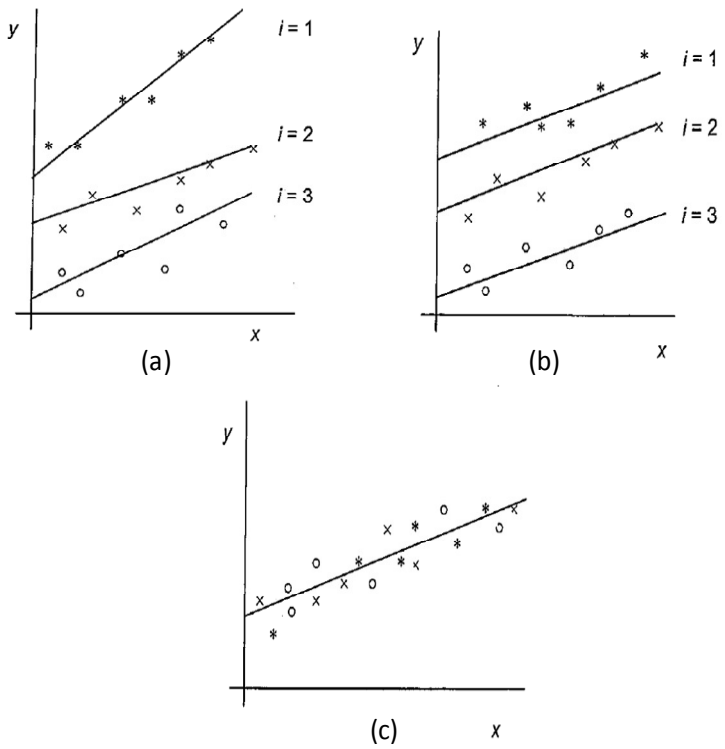


Figure 5 31 Three models for Simple Linear Regression with groups: (a) Separate Lines model, (b) Parallel Lines model and (c) Single Line model

In order to be able to include blocking as a factor as well, General Linear Regression is used to examine the relationship between total metals (K, Ca, Mg, Na, Fe and P) and the volatile combustion peak temperatures for different treatments and different parts (stems and leaves) of SRC willow.

5.6.4.2.3 General Linear Regression

General Linear Regression is used to fit a specific model using mathematical notations. This model gives flexibility in specifying the factors, variables and interactions to be fitted and also gives freedom in which order all the components are added into the model. For example the model to look at the effect of total metals on volatile combustion peak temperatures for different treatments of SRC willow is explained here. Three mathematical notations are used to specify the model as illustrated in Model 1 and Model 2 (which is a simplified version of Model 1)

Block + Metals + Treatment + Metals.Treatment (Model 1)

Can also be written as;

Block + Metals*Treatment (Model 2)

where:

"plus (+)" indicates the addition of various components (variables or factors)

"dot (.)" denotes the interaction between one or more components

"star (*)" provides a shorthand notation that will be expanded internally into each of the main components and their interactions

The linear model that would best fit the data can be decided using General Linear Regression using the following procedure:

1. If the Fpr of Metals.Treatment is <0.05, then there is an interaction between metals and treatments and hence the *Separate Lines mode*l (Model 1 or 2) is accepted. If Fpr is > 0.05 then go to 2
2. This is the *Parellel Lines mode*l from which the interaction has been removed hence the model is Block + Metals + Treatment. If Fpr of all three components is <0.05, then the model is accepted but if the Fpr of metals is <0.05 but that of block and treatment is > 0.05, then go to 3.
3. This is the simplest of the 3 models, *Single Line mode*l and will only focus on the metals (explanatory variable) and volatile combustion peak temperature (response variable).

   The Fpr for blocks is >0.05 for most of the analysis done in this study but it is still used as a factor in order to account for the background variation due to blocking hence giving a better coefficient of determination (r^2).

5.6.5 Results and Discussion of Regression Analysis for combustion studies.

5.6.5.1 Correlation between metals and volatile combustion peak temperature

In order to study the catalytic effect of inorganic metals (Ca, K, P, S, Mg and Na) on the volatile combustion peak temperature of stems and leaves for all the treatments for all the sampling times, a correlation analysis was done using *Pearson's correlation test* in Genstat. In this analysis, the effect of each metal on the other metals was also determined. The correlation coefficients are listed in Table 5.27. The shaded numbers indicate that there is a strong correlation.

Table 5 27 Correlation coefficients of metals and volatile combustion peak temperatures (T_{vm})

	T_{vm}	Ca	K	P	S	Mg	Na
Leaves							
T_{vm}	-						
Ca	**0.5771**	-					
K	-0.4412	**-0.6807**	-				
P	**0.5105**	**0.7783**	**-0.6139**	-			
S	0.2152	0.3201	0.0045	0.2121	-		
Mg	**0.5583**	**0.9186**	**-0.7186**	**0.7098**	0.1983	-	
Na	0.0199	0.2079	-0.1417	0.0582	-0.1933	0.2374	-
Stems							
T_{vm}	-						
Ca	0.1177	-					
K	-0.4141	-0.012	-				
P	-0.071	0.1948	**0.6592**	-			
S	-0.2045	0.1217	**0.6777**	**0.6252**	-		
Mg	0.0818	**0.5274**	0.2953	**0.6439**	0.4247	-	
Na	0.0255	0.3397	0.2622	0.3473	**0.6573**	0.3812	-

For the leaves, a number of fairly strong correlations have been found for metals with volatile combustion peak temperature while no strong correlations are found for the stems. Correlation coefficients fall between -1 and +1. Coefficients > [0.5] are considered to indicate a strong correlation. A strong positive correlation is seen where the increase of one variable causes the increase of the other variable and vice versa while a negative correlation is seen when the increase of one variable causes the decrease of another variable and vice versa.

For leaves, Ca, P and Mg show fairly strong positive correlations with volatile combustion peak temperatures. Ca shows a strong negative correlation with K and a strong positive correlation with Mg. K shows a strong negative correlation with Mg and P while P shows a strong positive correlation with Mg.

For the stems, no strong correlations are seen of the metals with volatile combustion peak temperatures. Ca shows a fairly strong positive correlation with Mg. K shows strong correlations with P and S. P shows strong positive correlations with S and Mg and S also shows a strong positive correlation with Na.

The correlations of Ca, K, P, S, Mg and Na with volatile combustion peak temperatures for both stems and leaves are also illustrated in Figure 5.33 a-f respectively. The range of total metal contents for stems is much narrower than that for leaves; hence there is less certainity in extrapolation of the line for the stems when conducting the correlation analysis.

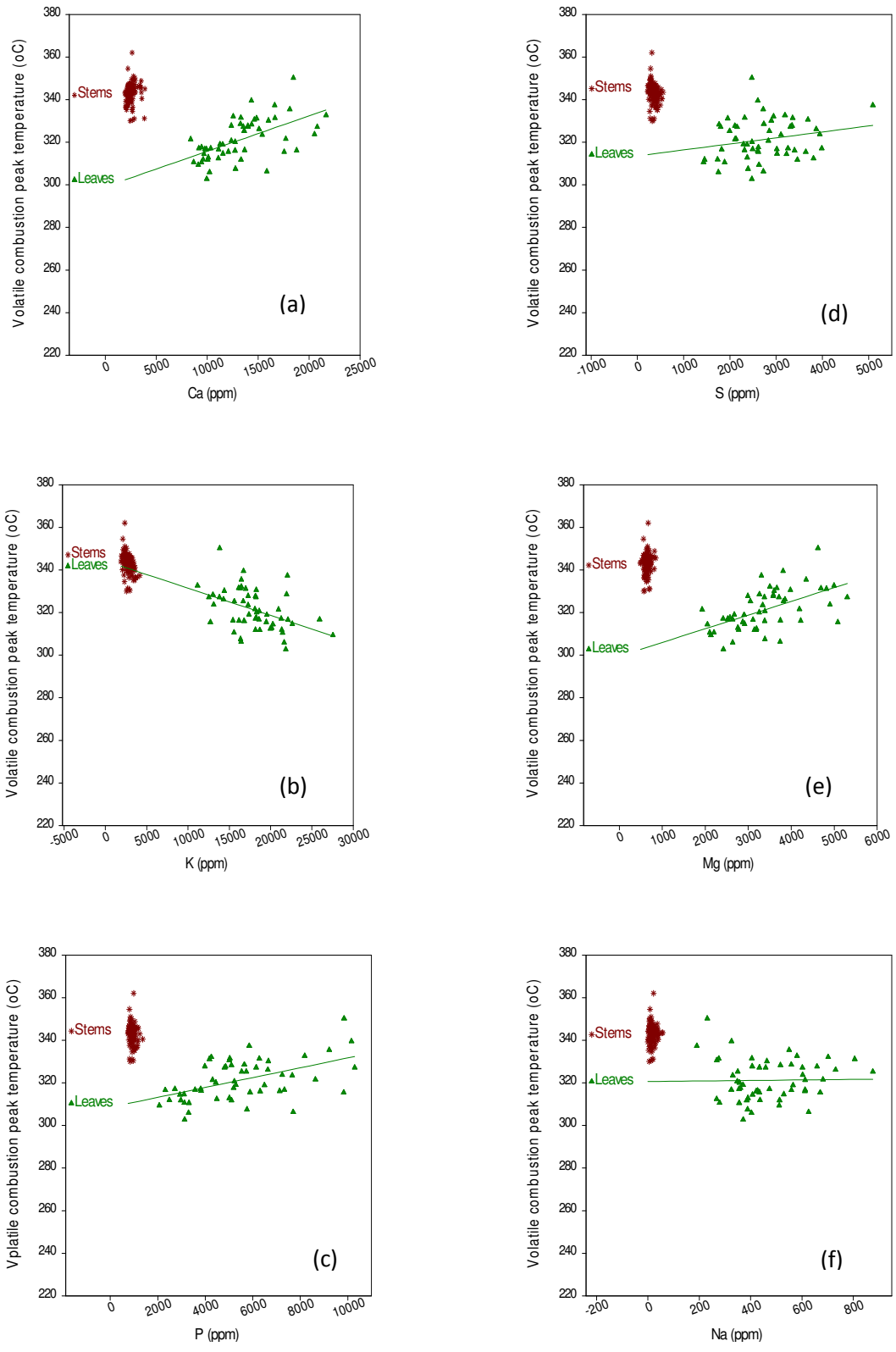


Figure 5 32 Correlation of (a) Ca, (b) K, (c) P, (d) S, (e) Mg and (f) Na with volatile combustion peak temperatures for leaves and stems

5.6.5.2 General Linear Regression Results

The effect of each individual metal with volatile combustion peak temperature has been studied in Section 5.6.5.1. In this section, the effect of total metals (Ca, Fe, K, P, Mg and Na) with volatile combustion peak temperature for different treatments and different parts (leaves and stems) of willow are examined. In these cases blocking has been incorporated into the model as well.

Percentage variance is the summary of how much of the variability of the data can be explained by a fitted regression model and can be calculated as (1-the ratio of Residual Mean Square to Total Mean Square) x100. Residual Mean Square is also known as the sample variance and Total Mean Square is means of all the squared differences between each individual data and the overall mean of all the data values. There is a good linear fit for all the data if the percentage variance is high (Payne, 2009).

5.6.5.2.1 Regression of total metals with volatile combustion peak temperatures for different treatments for leaves

Following the procedure in Section 5.6.4.1.2, a single line regression graph is plotted in Figure 5.34 to study the effect of volatile combustion peak temperature with total metals since the Fpr of blocks and treatments both were >0.05 in leaves. In this case metals is the explanatory variable and volatile combustion peak temperature is the response variable. The percentage variance accounted for is 20.5^{+}/- 8.25 and hence is not a very good linear fit.

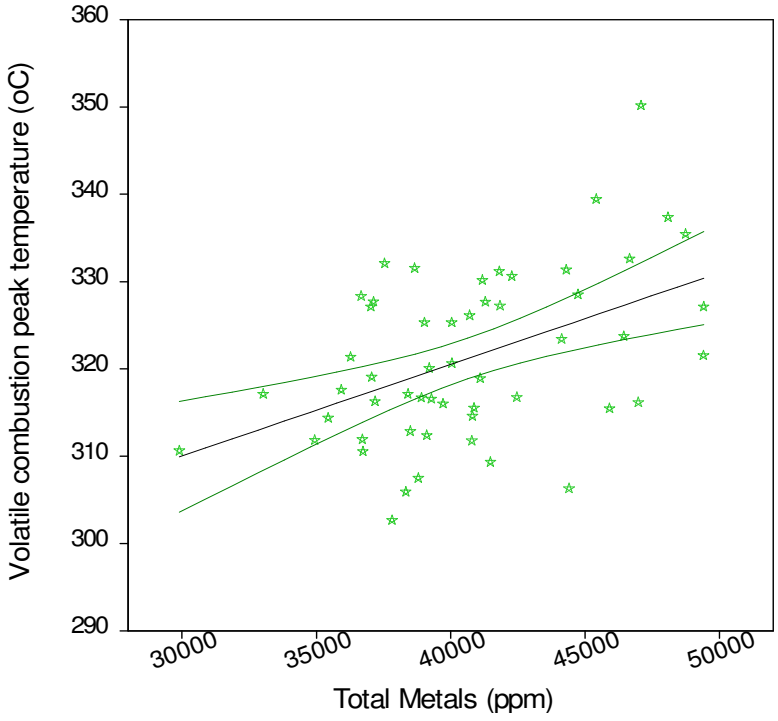


Figure 5 33 Single Line Regression of total metals with volatile combustion peak temperature for all 6 treatments for leaves

5.6.5.2.2 Regression of total metals with volatile combustion peak temperatures for different treatments for stems

A single linear regression graph is also plotted in Figure 5.35 to study the effect of total metals on volatile combustion peak temperature (since all the Fpr except for the one for metals are >0.05). For the stems, a slight negative correlation is seen and the percentage variance (4.5^{+}/-4.61) is very small indicating that the linear fit is very bad.

In the previous two cases, the effect of total metals on the volatile combustion peak temperatures was studied taking into account the different fertilizer treatments for leaves and stems individually, while in the next case only stems and leaves are taken into account by overlooking the application of different fertilizer treatments.

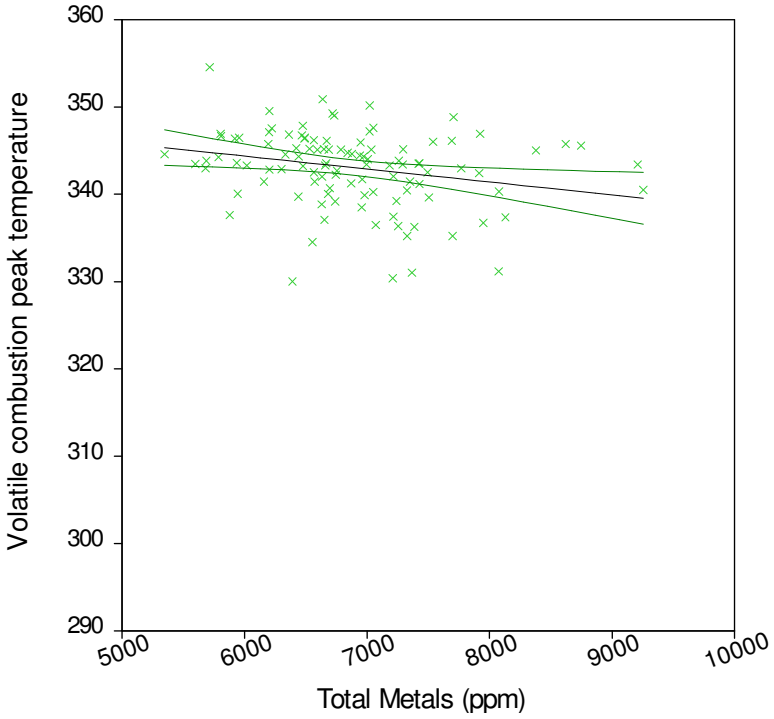


Figure 5 34 Generalised Linear Regression of total metals with volatile combustion peak temperature for all 6 treatments for stems

5.6.5.2.3 Regression of total metals with volatile combustion peak temperatures for different parts (leaves and stems)

A separate lines model is used for looking at the effect of total metals on volatile combustion peak temperature for leaves and stems of the willow. The model used is illustrated in Table 5.17. The percentage is very high 75.6^{+}/- 6.08 indicating that it is a relatively good linear fit. Peak volatile temperatures for leaves show a positive correlation while that of stems show a negative correlation.

Table 5 28 General Linear Model for Metals and Parts for SRC willow

	Metals	Parts	Metals.Parts	Block
Fpr	<0.001	<0.001	0.003	0.062
Percentage variance	75.6 +/- 6.08			
Generalised Linear Model	Separate Lines Model - (Blocks + Metals*Parts)			

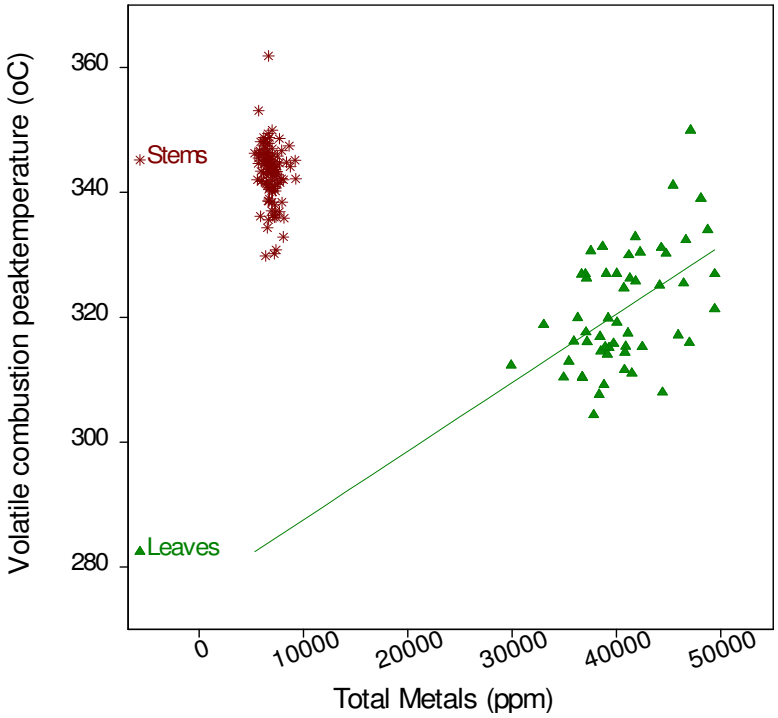


Figure 5 35 Generalised Linear Regression of total metals with volatile combustion peak temperature for stems and leaves

5.6.6 Discussion and Conclusions for TGA Combustion of SRC Willow

During the combustion of SRC willow, it is seen that leaves have a lower (311-330^{o}C) volatile combustion peak temperature compared to stems (33-350^{o}C). The volatile combustion peak temperature for leaves increases with sampling time due to the effect of changing concentration of some metals in the fuel.

Correlation co-efficient calculations for metals and volatile combustion peak temperatures showed that the volatile combustion peak temperature of SRC willow increases with increasing Ca, P and Mg. Some of the metals also show correlation with each other. As the total metals content of leaves increases, the volatile combustion peak temperature also increases while for the stems, an increase in total metals content leads to a decrease in volatile combustion peak temperature. This may indicate that the total metals in leaves are more volatile compared to stems.

Chapter 6

Combustion characteristics and combustion related problems of different species of the genus *Salix*

6.1 Introduction

The agronomy of SRC willow has been studied in Chapter 5 but farmers in the UK are recently showing great interest in breeding different genotypes of willow to improve yields and fuel quality. It is very feasible to do so with willow since it has a wide variety of genotypes, almost 350-500 species globally and it can easily be cross-bred. All the species of willow do not necessarily make good fuels but some of the species have highly desirable fuel properties. 80 years ago, a wide variety of willow species from around the world except Australia were captured in the National Willow Collection which was established at Long Ashton Research Station in Somerset UK which has since then expanded to house approximately 1500 different species of willow (Trybush et al., 2008).

This study is an initial exploration of some of the fuel properties of a variety of willow species from the National Willow Collection grown at Rothamsted Research to see the variation in desirable fuel traits. As part of a large study conducted for the UK Supergen Bioenergy Consortium (www.supergen.bioenergy.net) activity, 99 different genotypes of willow were taken but from those only a subset of 6 genotypes with highest and lowest cellulose, hemicelluloses and lignin were studied here. Fuel characterisation, ash behaviour studies, grindability tests, combustion tests, (Thermogravimetric Analysis (TGA) and single particle burning tests) and pyrolysis tests, (TGA and Pyrolysis Gas Chromatography-Mass Spectrometry (Py GC-MS)) were conducted on these species.

This is a very small study and a great deal more work needs to establish a statistically significant database in order to identify how different species of willow can be bred to produce good fuels. However, this initial study has resulted in conclusions which have identifief areas worthy of further investigation.

6.2 Materials and Experimental

6.2.1 Materials

The samples used for this study are detailed in Section 3.2.5.2. Six different genotypes of SRC willow were selected on the basis of highest and lowest cellulose, hemicellulose and lignin contents from results of analysis of samples taken in 2008. The same accessions were sampled again in 2011 and are also studied here. However biochemical composition is variable with age and overwinter of SRC willow and hence the samples from 2011 may not have the same biochemical composition trend as those from 2008. All the analysis except for the grindability tests have been conducted using particle size <600 µm. It was ensured that the same particle size was used for the 2011 samples by sieving the samples through a 600 µm sieve.

6.2.2 Experimental

All the experiments conducted on the samples are detailed in Section 3.3. Some experiments including the determination of the ash composition, ash fusion and ash melting tests and grindability tests were not carried out for *S.elaeagnos Scop* because there was insufficient sample. This was the result of poor growth of the crop in 2011. Proximate, ultimate and metal analyses were determined for the samples. The biochemical composition data was provided by IBERS. For the 2008 samples, the biochemical composition was determined using specific models as detailed in Section 3.3,4,1 while the biochemical composition for the 2011 samples was determined using wet chemistry according to Section 3.3.4.2. For the 2008 samples, ash composition was calculated from the metals in the fuel which were provided by Rothamsted Research while the ash composition was calculated from the metals at TES Bretby for the 2011 samples. Grindibility tests were conducted for the 2011 samples to determine how easily each species can be reduced in size. Ash fusion tests were also conducted under oxidising atmosphere for the 2011 samples to determine the temperatures of the different stages of ash deformation. Further ash melting tests were conducted by STA-MS to determine the evolution of intermediate species during the oxidation of ash and to compare the different stages of ash deformation for the two methods. TGA pyrolysis and Py GC MS (for 2008 samples

only) tests were conducted to look at the pyrolysis profiles and to detect the pyrolysis products respectively. TGA combustion tests were also conducted for all he samples to look at peak volatile release and char combustion temperatures. Single particle burning experiments were performed for the 2011 samples and ignition delay, and the duration of volatile release and char burnout were determined.

6.3 Results and Discussion

6.3.1 Fuel Characteristics

From the results in Table 6.1, it is observed that the genotype with the highest lignin content (*S.elaeagnos Scop*) has the highest ash content. The genotype with the lowest lignin content (*S.viminalis x S.schwerinii*) has the lowest ash content. *S.mielichhoferii Saut* from *2008* has the lowest calorific value; this is a result of the lowest carbon content and the highest oxygen content (Jenkins et al., 1998). Figure 6.1 illustrates the trends for the biochemical composition for the two years. The solid and dashed lines represent the samples from 2008 and 2011 respectively. The trends for the 2008 samples seem to have disappeared for the hemicellulose content from 2008 to 2011 but appear to be the same for the cellulose and lignin contents for the two years' samples. The corresponding biochemical compositions are listed in Table 6.1. The trend for the hemicelluloses content could have disappeared over the years or over the winter since the 2008 samples were taken in December while the 2011 samples were taken in February, although the trends could also be different due to the variation in methods for analyzing the biochemical composition. It is also observed that there are smaller variations in biochemical composition between the different species from 2011 compared to 2008. The cellulose, hemicelluloses and lignin contents vary within ranges of 33-55, 7-15 and 15-23 % respectively for the 2008 samples while they vary within the ranges of 38 - 48, 11 – 15 and 14 – 19% respectively for the 2011 samples. The biochemical composition does not add up to a 100% because the remaining mass includes some cell-wall bound water remaining even with oven drying along with some ash, some hydroxycinnamic acids (typically <1% DW (dry weight)), some proteins and the remains of other cell components. Also the values of cellulose, hemicellulose and ADL (Acid Detergent Lignin) are only estimates and ADL (method for measuring lignin) is most likely to measure

only 50% of the true lignin content and the ADF (Acid Detergent Fibre) (method for measuring cellulose and hemicellulose) fraction will have lost small amounts of cellulose and still contains some CS sugar The variation in ash content, 1-3 % for the different species is comparable for the two years

Table 6 1 Proximates, ultimates and biochemical compositions of the six different genotypes for the two years

Analysis	*S.aurita L.*		*S.viminalis x S.schwerinii*		*S.eriocephala Michx.*		*S. drummondiana Barratt ex Hook.*		*S.mielichhoferii Saut.*		*S.elaeagnos Scop.*	
	Dec-2008	**Feb-2011**	**Dec-2008**	**Feb-2011**	**Dec-2008**	**Feb-2011**	**Dec-2008**	**Feb-2011**	**Dec-2008**	**Feb-2011**	**Dec-2008**	**Feb-2011**
C (% daf)	53.65	49.33	53.58	49.52	53.68	49.57	51.98	51.00	46.13	50.62	54.27	51.01
H (% daf)	6.73	6.00	6.81	5.99	6.34	5.95	6.47	6.03	5.80	6.12	6.85	6.36
N (% daf)	0.95	0.57	0.81	0.45	1.02	0.36	0.86	0.85	0.57	0.66	0.89	1.25
O (% daf)[a]	38.67	44.10	38.80	44.04	38.96	44.12	40.69	42.12	47.50	42.60	37.99	41.38
Moisture (% ar)	6.16	2.73	6.59	2.72	4.96	2.89	4.74	2.72	5.46	2.26	6.05	5.65
Volatiles (% ar)	75.77	78.35	75.89	79.09	77.28	79.53	75.25	76.70	76.00	79.00	73.94	73.31
Fixed carbon (% ar)[a]	16.57	17.33	16.40	16.82	16.20	15.57	18.31	18.95	16.95	16.97	17.13	17.79
Ash (% ar)	1.50	1.59	1.11	1.37	1.56	2.01	1.71	1.63	1.59	1.77	2.88	3.25
HHV (MJ/kg db)[b]	21.50	19.28	21.61	19.39	21.33	19.24	20.56	20.00	17.98	19.81	21.41	19.74
Biochemical Composition												
% Hemicellulose	7.35	15.07	13.29	13.95	9.14	14.70	13.77	11.51	15.09	11.47	9.80	n.a
% Cellulose	50.02	43.92	52.98	47.80	54.06	48.03	33.52	38.34	42.22	43.57	46.56	n.a
% Lignin	18.40	18.41	15.49	15.46	18.05	14.79	22.17	18.42	18.62	18.35	27.13	n.a

[a] Calculated by difference

[b] Calculated using Equation 3.5

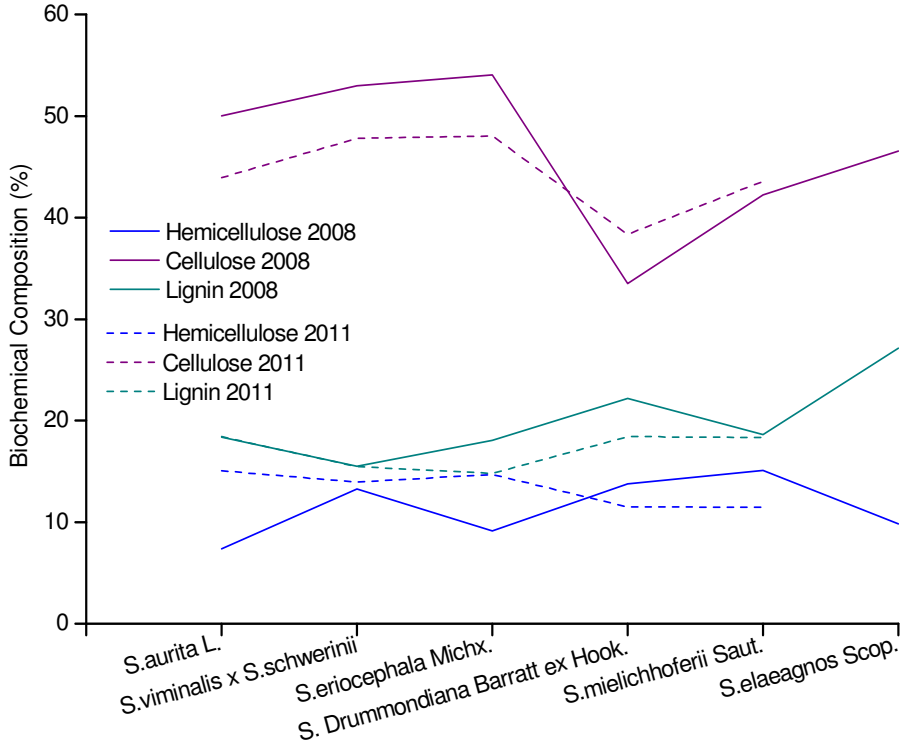


Figure 6 1 Biochemical Composition for the 6 genotypes for 2008 and 2011 samples

6.3.2 Ash Composition and Behaviour

6.3.2.1 Ash Composition

From the results in Table 6.2 it can be seen that CaO, K_2O, MgO, P_2O_5 and SO_3 contents are very high in these ashes. The trends followed by these genotypes for the two years are plotted in Figure 6.2. The solid and dashed lines represent samples from 2008 and 2011 respectively. All the metals except CaO follow a similar trend for 2008 and 2011 samples. The CaO, K_2O, MgO, Mn_3O_4, P_2O_5 and SO_3 contents in the ash from the 2008 samples are higher while the Al_2O_3, Fe_2O_3 and Na_2O contents are lower than those in the 2011 samples. The alkali index which is calculated according to Equation 4.1 indicate that all the genotypes except *S.elaeagnos Scop* have an alkali index < 0.17 kg alkali/GJ (Bryers, 1996). This is the lower threshold value for determining the fouling tendency of a fuel and hence it indicates that these genotypes except *S.elaeagnos Scop* which has an alkali index of 0.32 kg alkali/GJ would not cause any fouling.

The base to acid ratio ($R_{b/a}$) which indicates the slagging tendency of the fuels is calculated according to Equation 4.2 and is > 1 for all the genotypes. P_2O_5 is also included in these calculations since it is present in abundance in the ashes of the genotypes and it also gives a good correlation with ash fusion temperatures (Baxter et al., 2012, Lolja et al., 2002, Vincent R, 1987). For coal the lower threshold value of $R_{b/a}$ (excluding P_2O_5) is 0.5, below which slagging does not take place while the upper threshold value is 1, above which slagging certainly takes place (IEA, 1994). The threshold values for biomass are not known as yet. However it is probable that all the genotypes have high tendencies of slagging. For the 2008 samples, SiO_2 is not included in the calculation for $R_{b/a}$ since it was not analysed, hence the $R_{b/a}$ values would be a bit lower than values reported in Table 6.2 However the SiO_2 content of the ash is expected to be <5% therefore the $R_{b/a}$ values will not change very much.

Table 6 2 Ash Composition and Slagging/Fouling Indices for the six different genotypes for the two years

Analysis	*S.aurita L.*		*S.viminalis x S.schwerinii*		*S.eriocephala Michx.*		*S. drummondiana Barratt ex Hook.*		*S.mielichhoferii Saut.*		*S.elaeagnos Scop.*	
	Dec-2008	**Feb-2011**	**Dec-2008**	**Feb-2011**	**Dec-2008**	**Feb-2011**	**Dec-2008**	**Feb-2011**	**Dec-2008**	**Feb-2011**	**Dec-2008**	**Feb-2011**
Al_2O_3	0.08	0.30	0.08	0.30	0.00	0.30	0.06	0.50	0.19	0.30	0.01	n.a
CaO	53.05	37.90	38.01	39.30	50.11	42.50	37.05	35.20	39.78	32.50	36.66	n.a
Fe_2O_3	0.07	0.30	0.08	0.30	0.06	0.20	0.15	0.40	0.19	0.30	0.07	n.a
K_2O	17.66	12.60	21.19	17.10	13.72	10.10	15.79	15.40	16.04	13.80	22.26	n.a
MgO	5.18	3.00	7.55	3.90	3.68	2.60	4.60	3.40	7.38	4.00	2.60	n.a
Mn_3O_4	2.44	1.20	1.18	0.60	0.33	0.20	0.92	0.60	0.32	0.30	0.06	n.a
Na_2O	0.09	0.80	0.14	1.00	0.23	0.60	0.00	0.60	0.00	0.50	0.19	n.a
P_2O_5	14.78	9.70	14.81	13.00	8.31	6.40	13.96	13.10	13.85	12.40	8.52	n.a
SO_3	7.33	3.60	8.32	5.20	7.65	4.00	8.05	5.20	7.59	4.00	6.12	n.a
SiO_2	n.a	2.00	n.a	1.60	n.a	1.60	n.a	3.80	n.a	1.70	n.a	n.a
TiO_2	0.00	<0.1	0.00	<0.1	0.00	<0.1	0.00	<0.1	0.00	<0.1	0.00	n.a
Total ash compounds	100.68	71.50	91.36	82.40	84.09	68.60	80.58	78.30	85.34	69.90	76.49	n.c
Slagging/Fouling indices												
Alkali index (kg Alkali/GJ)[a]	0.13	0.11	0.12	0.13	0.11	0.12	0.14	0.13	0.15	0.13	0.32	n.c
Base to acid ratio[b]	5.12[c]	4.51	4.50[c]	4.11	8.16[c]	6.67	4.11[c]	3.14	4.52[c]	3.52	7.24[c]	n.c
Base percentage[d]	76.06	54.60	66.98	61.60	67.80	56.00	57.58	55.00	63.39	51.10	61.77	n.c

[a] Calculated using Equation 4. [b] Calculated using Equation 4.2

[c] SiO_2 not included in the calculation

[d] Sum of all the basic components (CaO, MgO, Na_2O, K_2O and Fe_2O_3)

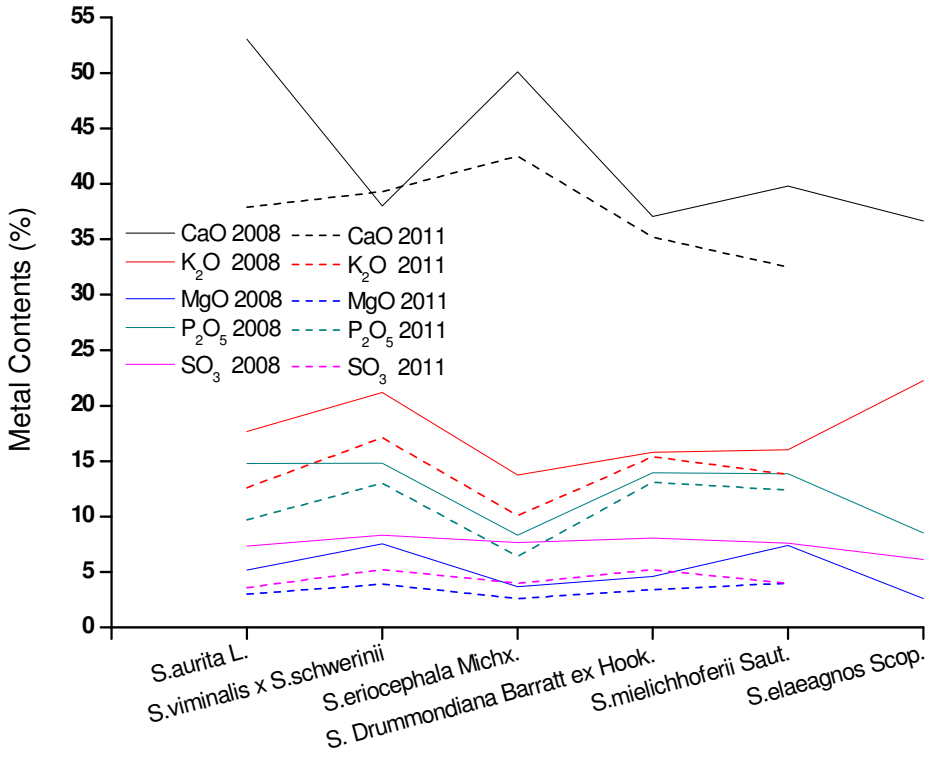


Figure 6 2 Major metal contents for the 6 genotypes for 2008 and 2011

6.3.2.2 Ash Fusion

Some alkali metals in the ash react with silica and sulphur to produce alkali silicates and sulphates which have low melting points and hence cause slagging and fouling on heat transfer surfaces and the heat recovery section respectively. Ash fusion tests were conducted under oxidising conditions according to Section 3.3.7 for all the genotypes except *S.elaeagnos Scop* and temperatures for the four crucial stages; shrinkage starting temperature (ST), deformation temperature (DT), hemisphere temperature (HT) and flow temperature (FT) were determined. Figure 6.1 shows an example the four crucial deformation stages of an ash test piece. Figure 6.1c shows the test piece at 1200^{o}C. At this temperature it is seen that the test piece is still very stable and not much deformation has taken place.

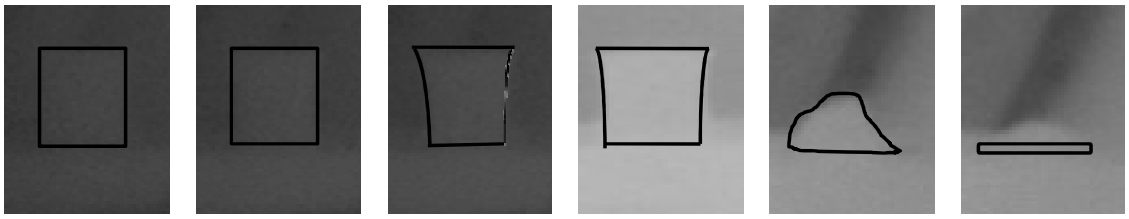


Figure 6 3 The 4 crucial stages of ash fusion test for *S.eriocephala Michx,* (a) Shrinkage, (b) Deformation, (c) Test piece at 1200°C (d) Hemisphere and (e) Flow

The ashes of the different genotypes are very stable and deformation starts at temperatures above 680°C. The temperatures for the four crucial stages for all the genotypes are listed in Table 6.3. Shrinkage and deformation of the ashes occur within a lower temperature range of 680-850°C, after which the sample is very stable until it reaches a temperature of approximately 1470°C and above when it suddenly collapses and melts. The sudden collapsing of the ash test pieces is quite abnormal since the ash test pieces of fuels like Miscanthus gradually deform and then melt (Baxter et al., 2012). SRC willow melting temperatures are very high compared to those reported for some agricultural residues such as PKE, olive and DDGS which soften at temperatures between 815 and 1310°C (as seen in Section 4.3.2) and also Miscanthus which softens at temperatures <1250°C (Baxter et al., 2012)

Table 6 3 Temperatures at the 4 crucial stages for the genotypes

Genotype	ST °C)	DT (°C)	HT (°C)	FT (°C)
S.aurita L	840	850	1525	1530
S.viminalis x S.schwerinii	820	835	1545	1550
S.eriocephala Michx	800	830	1475	1485
S. drummondiana Barratt ex Hook	690	710	1540	1540
S.mielichhoferii Saut	685	710	1540	1550

ST Shrinkage Temperature HT Hemisphere Temperature

DT Deformation Temperature FT Flow Temperature

For the base percentages reported in Table 6.3, hemisphere temperatures can be as low as 1100°C, as reviewed by (Bryers, 1996). Bryers plotted a regression analysis for hemisphere (softening) temperature against the base percentage for coals and some biomass as shown in Figure 6.4.. From this analysis, it was concluded that biomass can be classified into the following three types: (Bryers, 1996)

1. Ashes with high potassium, high silica and low calcium usually the case for grasses
2. Ashes of wood derivatives, pits and shells with high calcium, high potassium and low silica
3. Ashes of manure containing high calcium and high phosphorous.

The hemisphere temperatures and base percentages of the genotypes were also plotted on the figure. It was found that the ashes of the genotypes of behave in a similar manner to that of the wood derivatives, pits and shells.

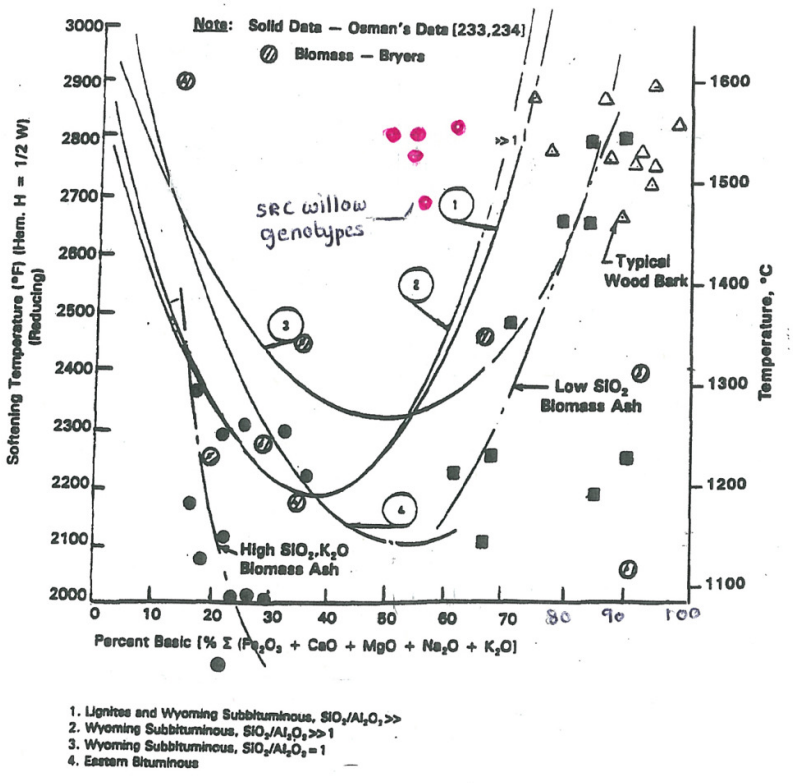


Figure 6 4 Hemisphere temperatures and base percentages of SRC willow genotypes plotted with Bryers data (Bryers, 1996)

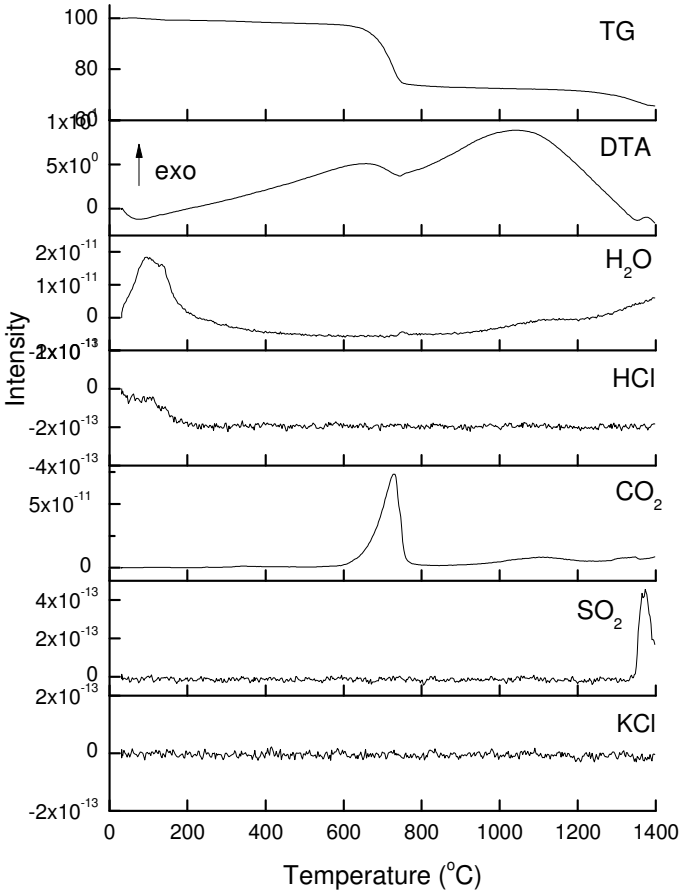
Ash fusion tests for the genotypes have only been performed under oxidising atmosphere. Previous studies, where tests have been done under both reducing and oxidising atmosphere, have shown that the hemisphere temperature is lower under reducing conditions compared to oxidising conditions (Baxter et al., 2012), typically by 100-200^{o}C. Low deformation temperatures result in deposition in boilers and provide a sticky surface onto which non-fused particles might stick.

6.3.2.3 Ash Melting Behaviour

Ash melting tests were conducted according to Section 3.3.8 to identify some of the common compounds that are formed during the combustion of biomass ash. STA tests has proved useful in previous studies to investigate the ash behaviour of Miscanthus (Baxter et al., 2012) and various straws (Arvelakis et al., 2004).

From Figure 6.5a-e, it is seen that for all the genotypes H_2O evaporates at <200^{o}C, CO_2 which is mainly from the dissociation of $CaCO_3$ is seen between 600-800^{o}C and finally SO_2 is seen at temperatures >1200^{o}C and is mainly a product of $CaSO_4$. This is in total agreement with literature which reported that at temperatures <850^{o}C, evaporation of moisture and dissociation of carbonates, such as $CaCO_3$ and $KHCO_3$ and K_2CO_3 occur to produce CO_2. Between 850 and 1150^{o}C, KCl is the most likely compound to be produced although some CO_2 might be detected in cases where SiO_2 and K_2CO_3 react. At temperatures between 1150 and 1400^{o}C, SO_2 which is produced from the dissociation of sulphates and some Cl is detected (Arvelakis et al., 2004, Baxter et al., 2012).

For Figures 6.5a, c, and e, a slight peak is seen for HCl at <200^{o}C and this is because of instability of the baseline. A slight peak for HCl is seen at temperatures > 1200^{o}C for *S.eriocephala Michx*, *S. drummondiana Barratt ex Hook* and *S.mielichhoferii Saut*. The evolution profiles of SO_2 and HCl seem to be linked to each other and appear to arise from similar dissociation processes. This is a bit strange since Cl is present in very small amounts (<0.02%). For *S.viminalis x S.schwerinii,* two distinct peaks are observed for CO_2. The first peak is the result of the dissociation of $CaCO_3$. For the second peak, some H_2O is also given off with the CO_2, which indicates the possible dissociation of HCO_3.



(a)

Figure 6 5 Mass loss, DTA and evolved species of STA ash melting tests of (a) *S.aurita L*

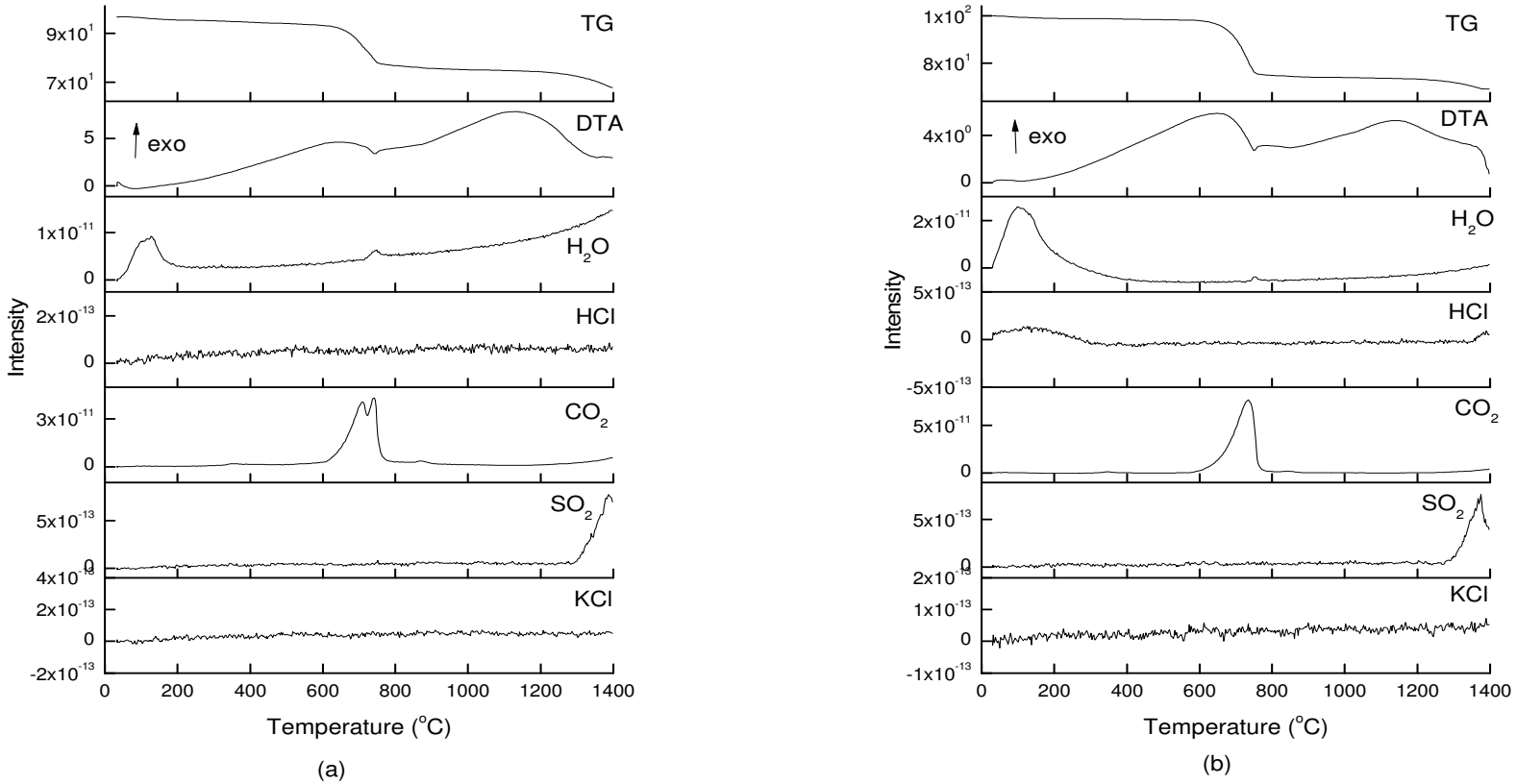


Figure 6 6 Mass loss, DTA and evolved species of STA ash melting tests of (a) *S.viminalis x S.schwerinii* and (b) *S.eriocephala Michx.*

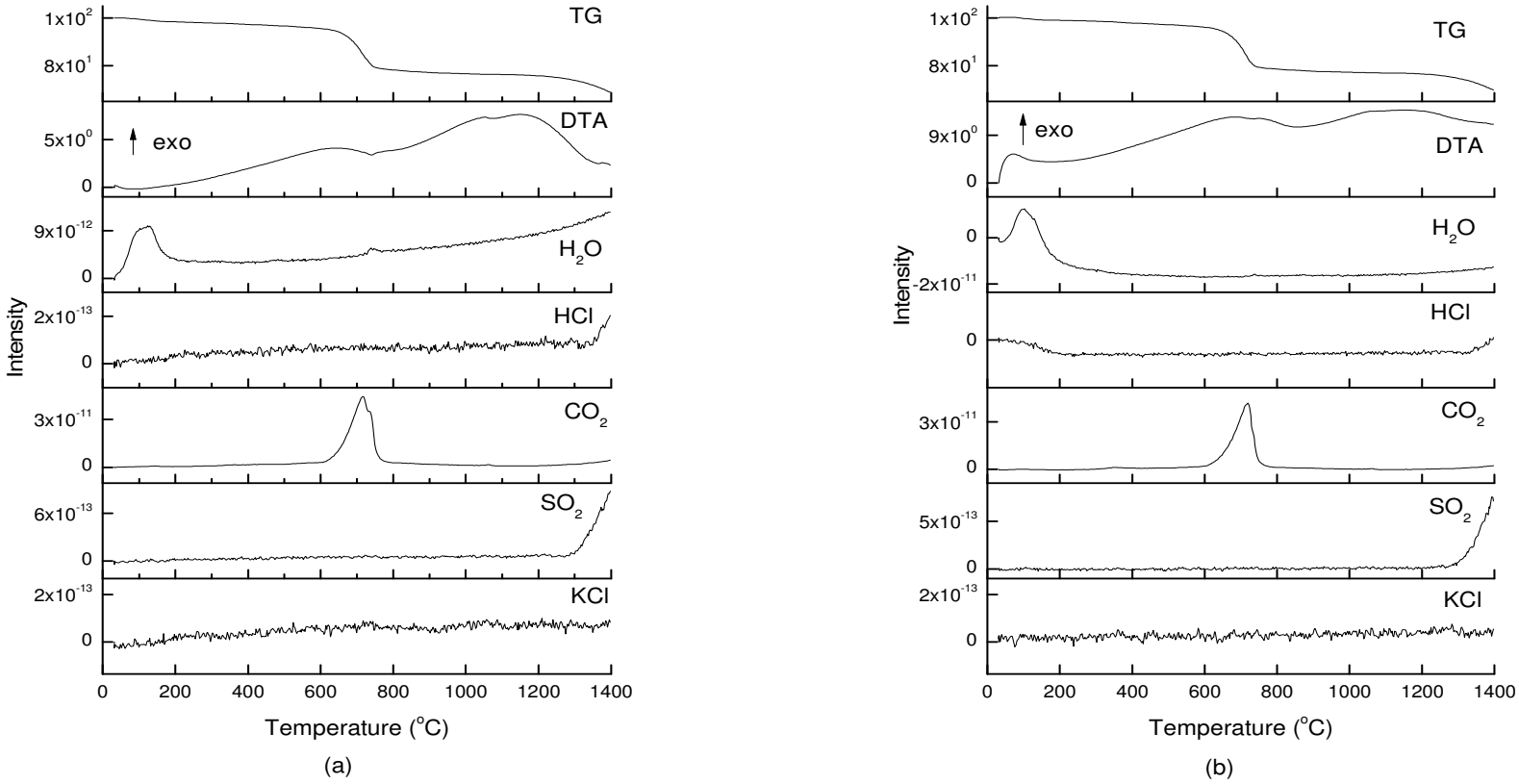


Figure 6 7 Mass loss, DTA and evolved species of STA ash melting tests of.and (a) *S. drummondiana Barratt ex Hook* and (b) *S.mielichhoferii Saut.*

Every time there is a dissociation reaction occurring in the ash, the DTA curve becomes endothermic. For all the genotypes we can see two distinct endothermic reactions, the first between 650 and 800^{o}C which is due to the dissociation of $CaCO_3$ and the other between 1200-1400^{o}C due to the dissociation of $CaSO_4$. An endothermic reaction is not observed for ash melting since all these ashes melt at temperatures >1400^{o}C as seen from the ash fusion tests. It is very unfortunate that the maximum furnace temperature is only 1400^{o}C.

From the TGA curves shown in Figures 6.5, 6.6 and 6.7, it is seen that evaporation of moisture occurs at <200^{o}C. Between 600 and 800^{o}C, a major mass loss occurs when the first endothermic reaction occurs which is due to the dissociation of carbonates. At temperatures >1200^{o}C, only part of the mass loss is seen which is due to the dissociation of sulphates since the samples are only heated to 1400^{o}C. For the H_2O curve, an increase in H_2O is seen between 1200 and 1400^{o}C which could be due to a shift in the baseline.

6.3.3 Grindability Tests

6.3.3.1 Hardgrove Grindability Index (HGI)

The HGIs of the samples were determined according to Section 3.3.5.1 and these were compared with some reference coals with known HGIs. These HGIs along with the amount of sample passing through the 75 µm sieve are reported in Table 6.4. Fuels with lower HGI are more difficult to grind compared to those with higher HGIs as shown in previous studies (Bridgeman et al., 2010). *S.elaeagnos Scop* shows good grinding conditions since it has an HGI of 50.9 and 9 % of the sample passes through the 75 µm sieve. It has better grinding conditions compared to two of the coals as well which have HGIs of 32 and 49. *S.mielichhoferii Saut* shows the poorest grinding conditions since it has an HGI of <0 and only 0.9 % of the sample passes through the 75 µm sieve.

Table 6 4 HGIs and amount of sample <75 µm

Sample	HGI	Mass <75 µm (%)
Coal	92.0	15.7
	66.0	13.2
	49.0	8.3
	32.0	5.8
S.elaeagnos Scop	50.9	9
S.aurita L	4.5	1.7
S. drummondiana Barratt ex Hook	2.0	1.3
S.viminalis x S.schwerinii	0.7	1.1
S.eriocephala Michx	0.1	1
S.mielichhoferii Saut	-0.5	0.9

Figure 6.8 shows the HGIs of the different genotypes compared to the different coals. The squares represent the coals while the triangles represent the different samples and their different colours of the triangles match the colours of the different samples shown in Figure 6.8. The HGIs of the different genotypes except *S.mielichhoferii Saut* fall within the calibration curve for the HGIs of reference coals and give a good correlation.

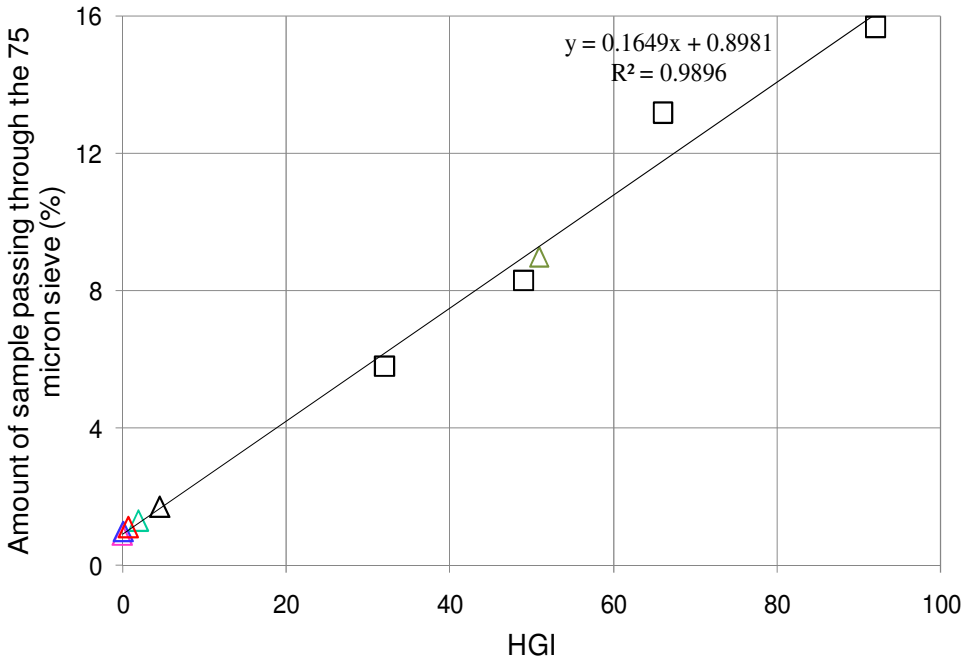


Figure 6 8 HGIs for reference coals and 6 different genotypes of SRC willow

6.3.3.2 Particle Size Distribution

Particle size distribution of the samples was determined according to Section 3.3.5.2. Figure 6.9 shows the particle size distribution of the four reference coals and the six genotypes of SRC willow. *S.elaeagnos Scop* shows similar distribution profiles to those of the coals indicating once again that it has good grinding properties while all the other genotypes show different profiles. 35 % of the mass of *S.elaeagnos Scop* passes through the 355 µm sieve while only < 10 % of the mass of the other genotypes pass through the 355 µm sieve. This makes *S.elaeagnos Scop* very attractive for use in power stations since its milling will be a less energy intensive process.

Previous studies have shown that torrefied biomass is easier to grind compared to raw biomass materials since the hemicellulose which forms structural linkages in the biomass material, breaks down during torrefaction and forms a material with lower strength and good grinding properties (Ciolkosz and Wallace, 2011). For experiments conducted on a laboratory scale, it has been reported that the energy required for grinding torrefied biomass is approximately 10-20 % of the energy required for grinding raw biomass material (Ciolkosz and Wallace, 2011).

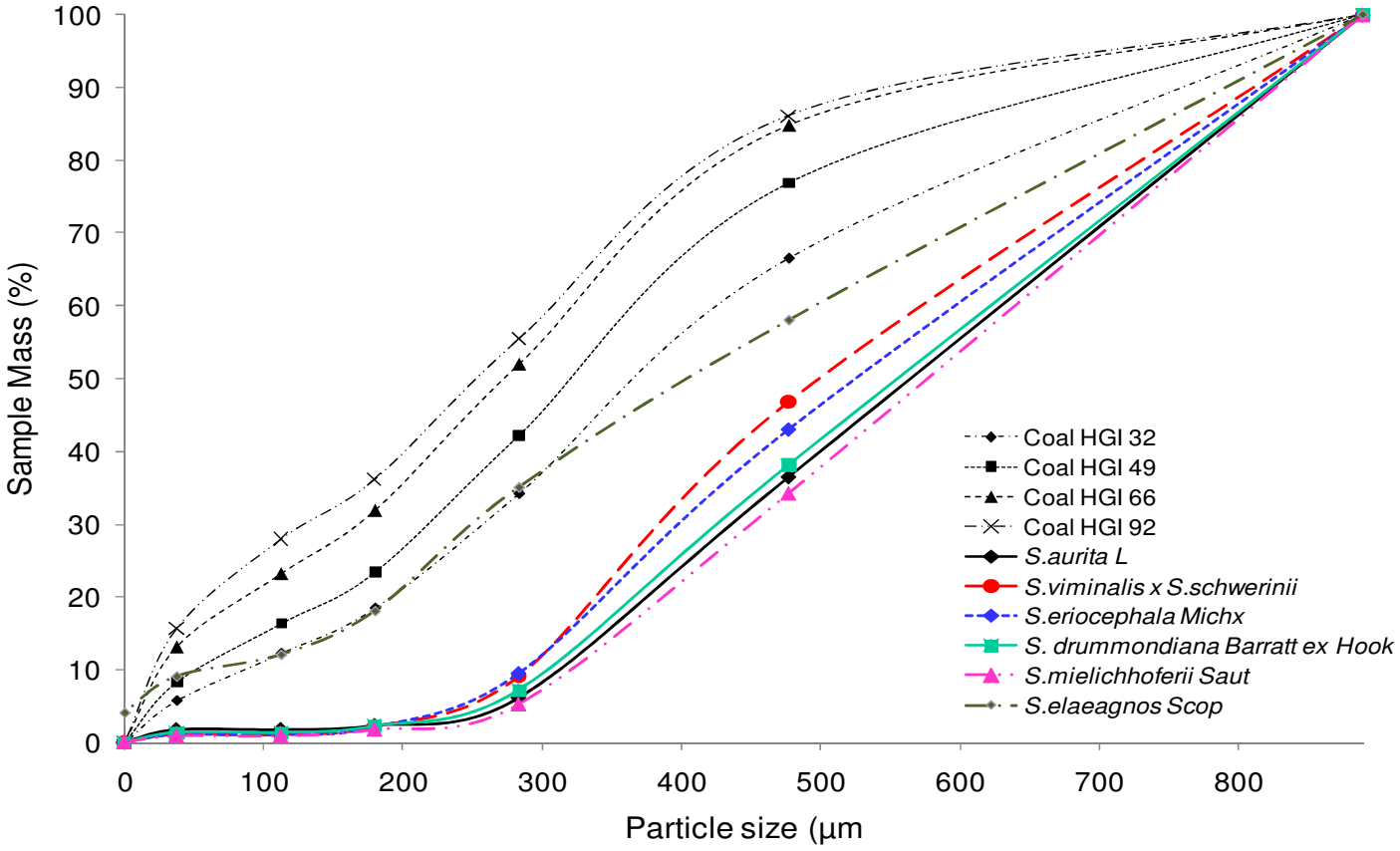


Figure 6 9 Particle Size Distribution of the reference coals and the six different genotypes of SRC willow

6.3.4 Scanning Electron Microscope

The six genotypes were examined under a scanning electron microscope and the images of the raw samples and dispersion of certain metals in the SRC willow samples were obtained. Only one of the images is presented here (*S.elaeagnos Scop)* while the rest of them are presented in Appendix E.

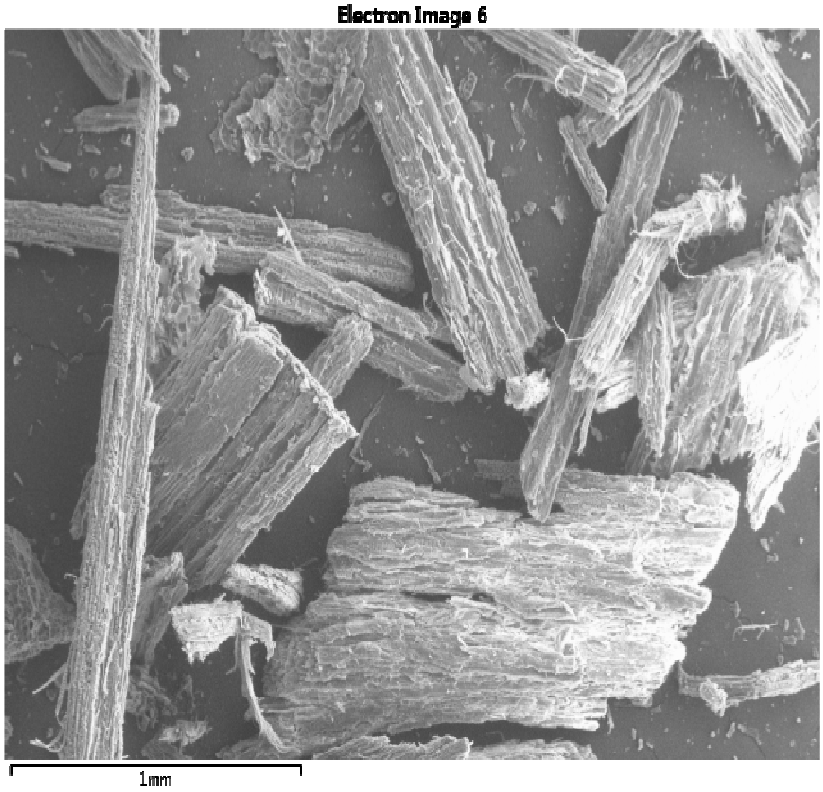


Figure 6 1 0 SEM image of raw sample of *S.elaeagnos Scop*

It is generally seen that the organic compounds like C and O are present throughout the sample. The few metals that are seen in *S.elaeagnos Scop* are seen in the biomass are, K, Ca, Mg and Na. K, Na and Mg are present in both the woody parts and bark of the SRC willow while interestingly enough Ca is only seen in the bark.

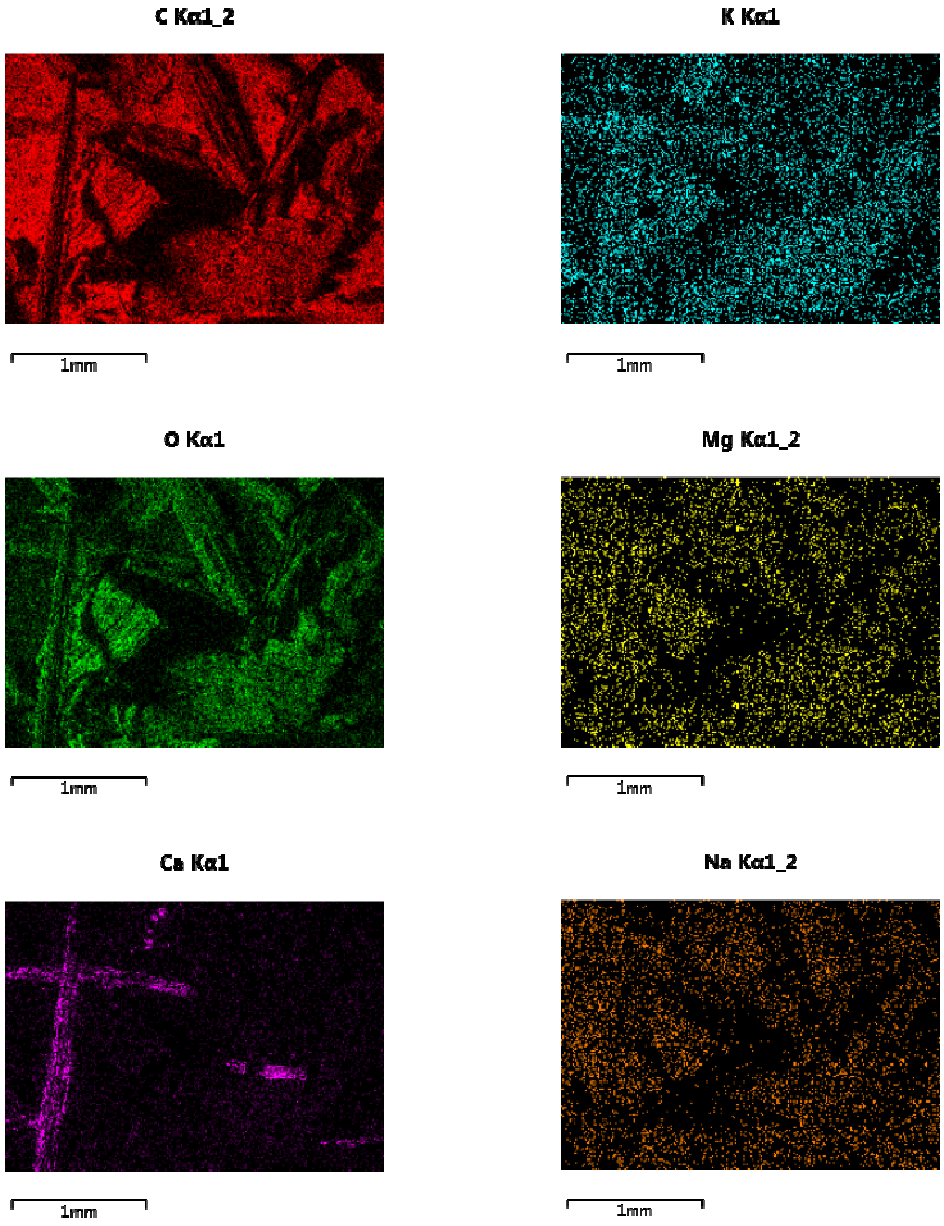


Figure 6 1 1 SEM images of metals dispersion in *S.elaeagnos Scop*

6.3.5 Pyrolysis studies

6.3.5.1 Thermogravimetric Analysis (TGA)

Pyrolysis tests were conducted with a heating rate of 10^{o}C/min to a temperature of 600^{o}C under helium for all the samples. Once pyrolysis was completed, the chars were then cooled and heated up to 600^{o}C but this time in air with the same heating rate.. Figures 6.12 and 6.13 show the mass loss and DTG curves for pyrolysis plotted against the temperature for the 2008 and 2011 samples respectively. The mass loss curves are presented as solid lines while the DTG curves are presented as dashed lines. The large drop in the mass loss curve indicates the release of volatile matter and the residue that remains is the char. The amount of char that remains after pyrolysis for both the 2008 and 2011 samples is approximately 23-40%. and 20-33% respectively. *S.viminalis x S.schwerinii* has the lowest char yield for both the 2008 and 2011 samples while *S.elaeagnos Scop* has the highest char yield for both years.

From the mass loss curve, a distinct shoulder on the left represents hemicelluloses decomposition and the larger distinct peak represents cellulose decomposition. Lignin decomposition occurs over a wide temperature range.. From Figures 6.12 and 6.13, it can be seen that hemicelluloses and cellulose decomposition occurs at between approximately 230-300^{o}C and 320-400^{o}C respectively for both year samples. The 2011 samples are more representative of model compounds of hemicelluloses, cellulose and lignin which have previously been pyrolysed to shown that hemicellulose decomposes over a temperature range of 220-315^{o}C and cellulose decomposes over a temperature range of 315-400^{o}C (Yang et al., 2007).

The peak temperatures for pyrolysis and char combustion are listed in Table 6.8. *S.elaeagnos Scop* from both 2008 and 2011 behaves very differently compared to the other genotypes. It has a peak temperature of 341.4 and 340.6^{o}C for the 2008 and 2011 samples respectively which is much lower compared to the peak temperatures of the other genotypes which are in the range of 359.5-362.8^{o}C and 362.8-364.7^{o}C for the 2008 and 2011 samples respectively.

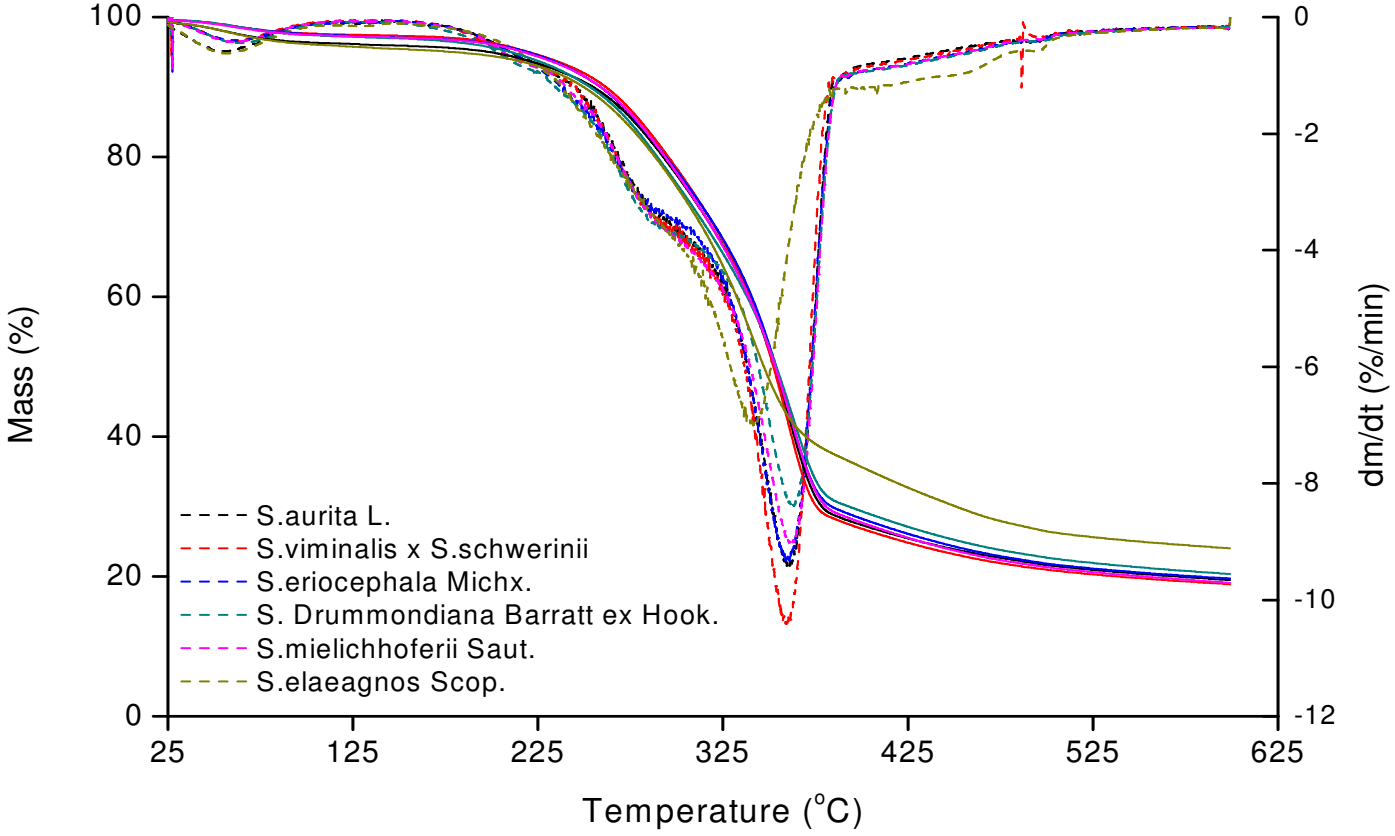


Figure 6 1 2 Mass loss curves and Derivative of mass loss (DTG) curves against temperature for the 2008 samples from TGA pyrolysis studies

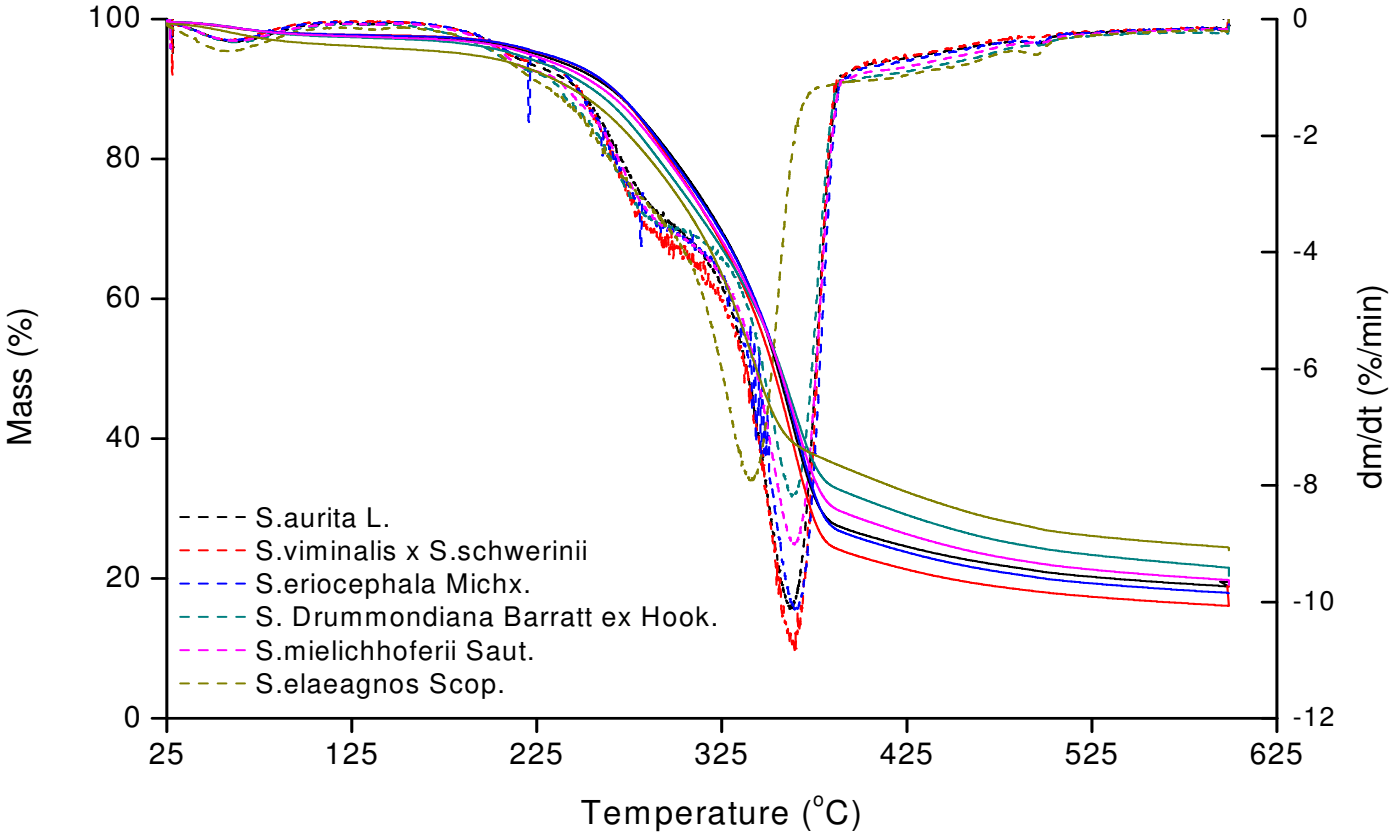


Figure 6 1 3 Mass loss curves and Derivative of mass loss (DTG) curves against temperature for the 2011 samples from TGA pyrolysis studies

6.3.4.1 Pyrolysis Gas Chromatography-Mass Spectrometry (Py GC-MS)

Py GC-MS analysis was only performed for the 2008 samples. The chromatograms produced from the Py GC-MS of the genotypes with (a) lowest and (b) highest hemicellulose, cellulose and lignin as listed in Table 6.1 are shown in Figures 6.14, 6.15 and 6.16 respectively. The assignment of the main peaks is made from the mass spectral detection library (NIST.05A MS) and with comparison to previous work ((Darvell et al., 2010, Fahmi et al., 2007b, Nowakowski and Jones, 2008, Nowakowski et al., 2007). The most likely precursors for the genotypes with lowest and highest hemicelluloses, cellulose and lignin are reported in Tables 6.5, 6.6 and 6.7 respectively. Most of the compounds detected are from the decomposition of lignocelluloses and include some esters, aldehydes, methoxyphenols and some furfural derivatives. At early retention times, decomposition products are mainly cracked products from cellulose monomers, while lignin decomposition products are observed at later retention times. The lignin in wood consists predominantly of two different aromatic nuclei; guaiacol (2-methoxyphenols) and syringol (2, 6-dimethoxyphenols). Guaiacol is mainly found in softwoods while guaiacol and syringol are both found in hardwood (Asmadi et al., 2011, Ingemarsson et al., 1999).

From Figure 6.14, it appears that peaks 13 (3',5'-dimethoxyacetophenone) and 14 (phenol, 2,6-dimethoxy-4-(2-propenyl)-) are highly sensitive to the hemicellulose content in the fuel. *S.aurita L* which has the lowest hemicelluloses (7.4%) content has a third of the amount of 3',5'-dimethoxyacetophenone and almost a fifth of the amount of 2,6-dimethoxy-4-(2-propenyl)- phenol compared to *S.mielichhoferii Saut* which has the highest hemicelluloses (15.1%) content. For the genotypes with the highest (54.1%) and lowest cellulose (42.2%) contents, no sensitivity is seen in the decomposition products. The lignin content of the genotypes also shows some sensitivity in the decomposition products. From Figure 6.16, it is seen that *S.viminalis x S.schwerinii* which has the lowest lignin (15.5%) content has a third of the phenol and approximately half the phenol, 2-methoxy- present in *S.elaeagnos Scop* which has the highest (27.1%).

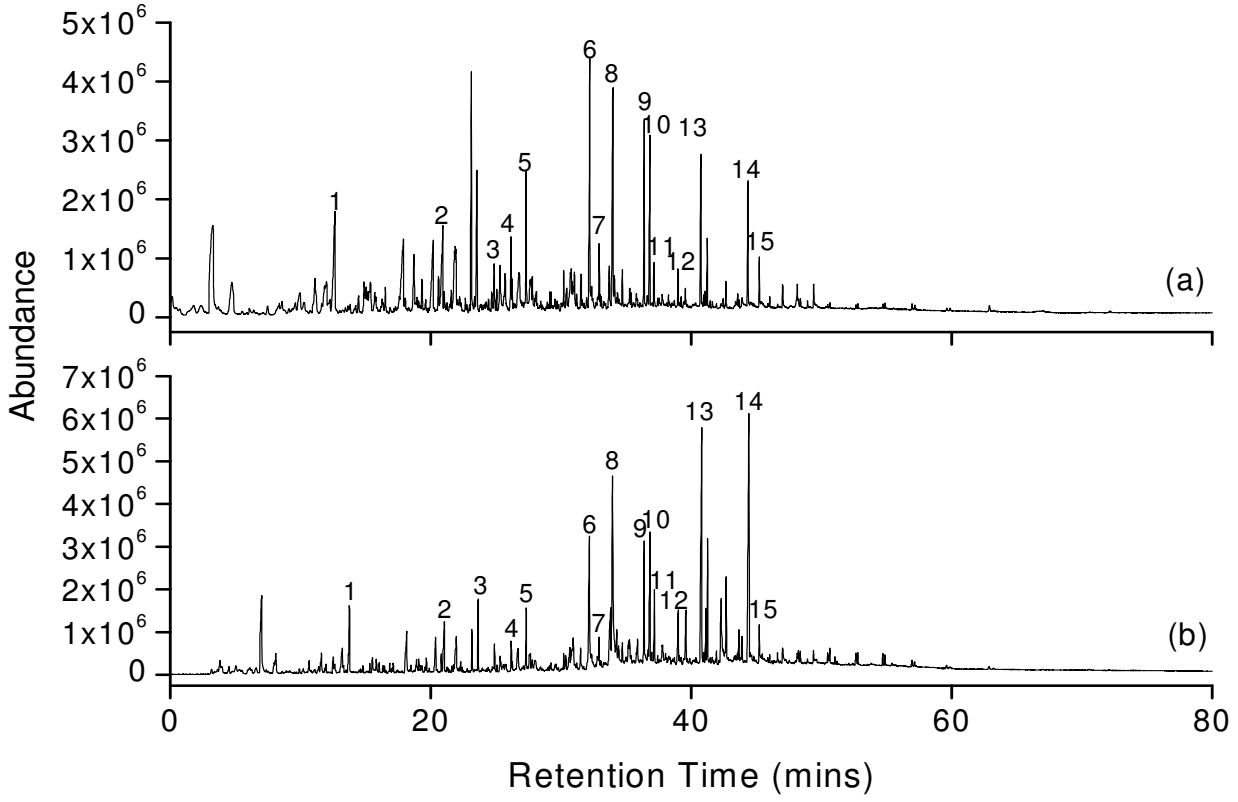


Figure 6 1 4 Figure 6.8 Py GC-MS chromatograms of (a) *S.aurita L* and (b) *S.mielichhoferii Saut* with lowest and highest hemicelluloses contents respectively

Table 6 5 Corresponding compounds for numbered peaks in Py GC-MS chromatogram of *S.aurita L and S.mielichhoferii Saut*

Peak	Compound	RMM	Marker	Area under the peak	
				Low hemicellulose	**High hemiicellulose**
				S.aurita L.	***S.mielichhoferii Saut.***
1	Furfural	96	Cellulose	6283383	5194553
2	Oxazolidine, 2,2-diethyl-3-methyl-	143	?	2352776	6542898
3	Phenol, 2-methoxy-	124	Guaiacol lignin	9631536	4728409
4	Phenol, 4-methyl-	108	Hydroxyphenyl lignin	4583612	2174529
5	Phenol, 2-methoxy-4-methyl-	138	Guaiacol lignin	7304012	3874486
6	2-Methoxy-4-vinylphenol	150	Hydroxyphenyl lignin	16267373	12521916
7	Eugenol	164	Guaiacol lignin	2183310	1360122
8	Phenol, 2,6-dimethoxy-	154	Syringol lignin	15150601	26922445
9	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	164	Guaiacol lignin	10012898	8832243
10	1,2,4-Trimethoxybenzene	1668	?	9432007	11238949
11	Vanillin	152	Guaiacol lignin	1585556	5140625
12	Benzene, 1,2,3-trimethoxy-5-methyl-	182	Syringol lignin	1537315	4372375
13	3',5'-Dimethoxyacetophenone	180	Lignin	8341580	30989323
14	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	194	Syringol lignin	6314405	29529770
15	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	182	Syringol lignin	2387289	2791295

Table 6 6 Corresponding compounds for numbered peaks in Py GC-MS chromatogram of *S. drummondiana Barratt ex Hook* and *S.eriocephala Michx*

Peak	Name	RMM	Marker	Area under the peak	
				Low cellulose	**High cellulose**
				S. Drummondiana Barratt ex Hook.	***S.eriocephala Michx.***
1	Furfural	96	Cellulose	5075226	3304209
2	2-Furanmethanol	98	Cellulose	1208955	947314
3	1,2-Cyclopentanedione	98	Lignin	6771391	5210416
4	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	112	Cellulose	1018176	3656301
5	Phenol, 2-methoxy-	124	Guaiacol lignin	3477642	2833873
6	Phenol, 2-methoxy-4-methyl-	138	Guaiacol lignin	2469388	1844757
7	2-Methoxy-4-vinylphenol	150	Guaiacol lignin	7494280	4856171
8	Phenol, 2,6-dimethoxy-	154	Syringol lignin	18322261	9325610
9	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	164	Guaiacol lignin	5392206	4470878
10	1,2,4-Trimethoxybenzene	168	?	6229835	5186199
11	Vanillin	152	Guaiacol lignin	1433887	2237205
12	3',5'-Dimethoxyacetophenone	180	Lignin	17344397	16518693
13	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	194	Syringol lignin	21085859	16520360
14	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	182	Syringol lignin	6260033	2409951
15	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	196	Syringol lignin	4615268	1134063

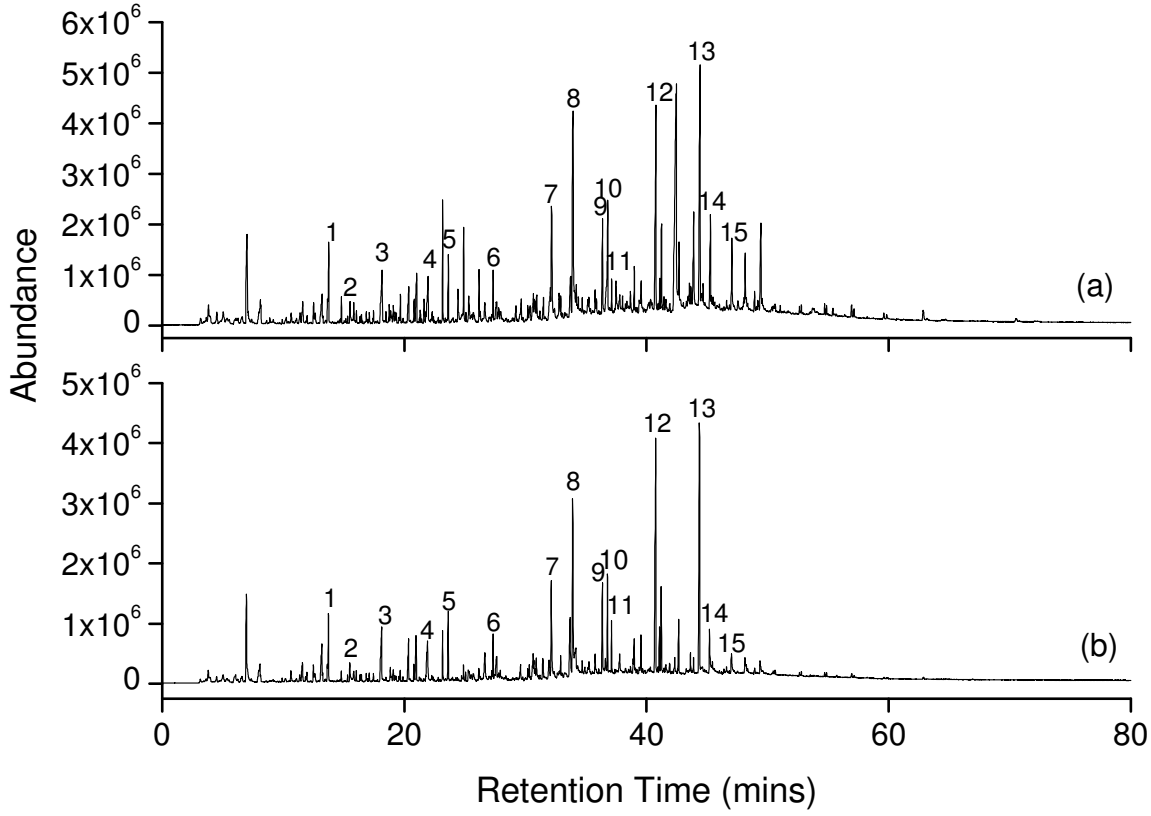


Figure 6 1 5 Figure 6.9 Py GC-MS chromatograms of (a) *S. drummondiana Barratt ex Hook* and(b) *S.eriocephala Michx* with lowest and highest cellulose contents respectively

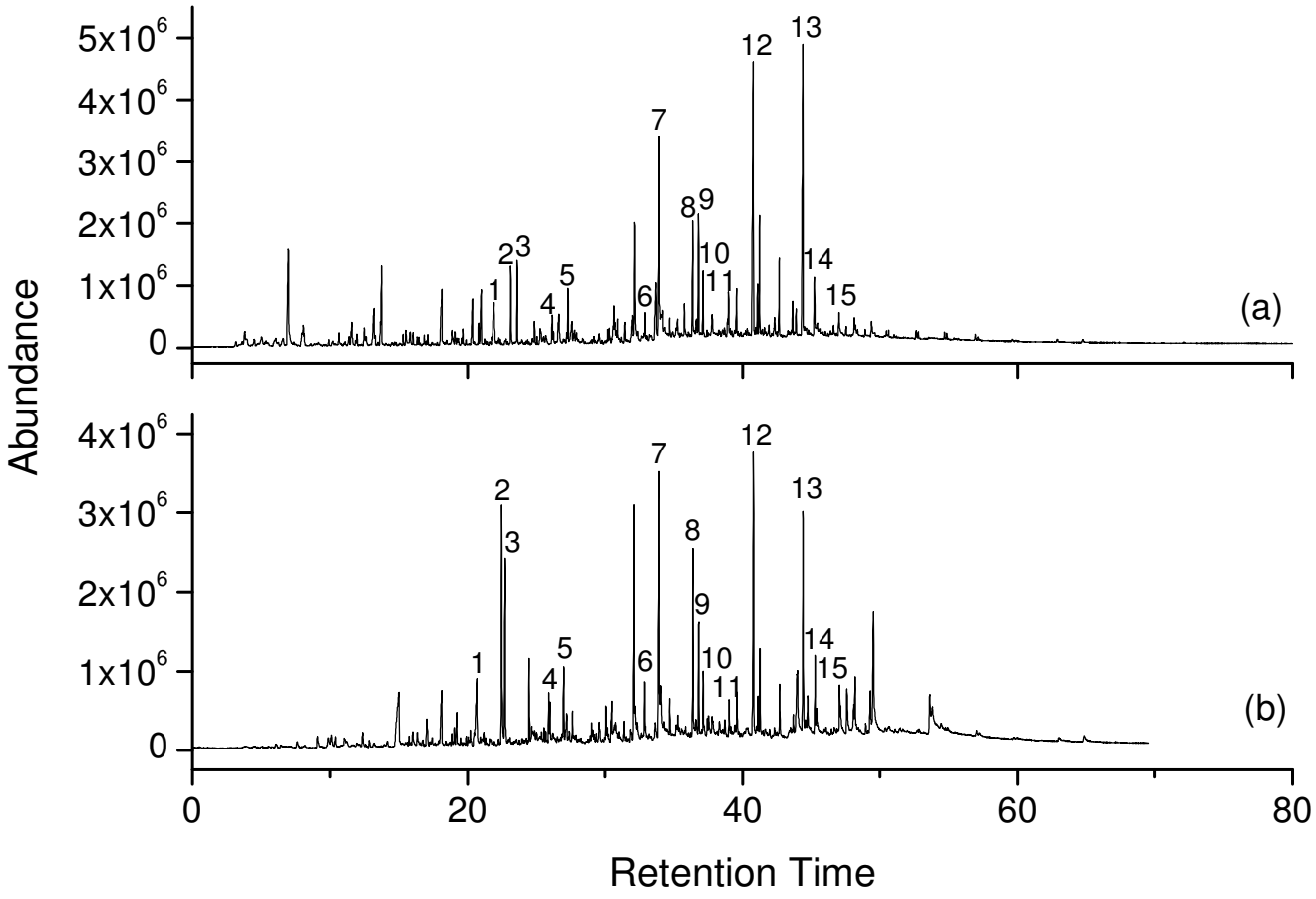


Figure 6 1 6 Py GC-MS chromatograms of (a) *S.viminalis x S.schwerinii* and (b) *S.elaeagnos Scop* with lowest and highest lignin contents respectively

Table 6 7 Corresponding compounds for numbered peaks in Py GC-MS chromatogram of *S.viminalis x S.schwerinii* and *S.elaeagnos Scop*

Peak	Compound	RMM	Marker	Area under the peak	
				Low lignin	**High lignin**
				S.viminalis x S.schwerinii	***S.elaeagnos Scop.***
1	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	112	Cellulose	4321638	4950170
2	Phenol	94	Lignin/Cellulose	3066824	11008235
3	Phenol, 2-methoxy-	124	Guaiacol lignin	3353020	8230446
4	Phenol, 4-methyl-	108	Hydroxyphenyl lignin	1713431	1676203
5	Phenol, 2-methoxy-4-methyl-	138	Guaiacol lignin	2101175	1136316
6	Eugenol	164	Guaiacol lignin	926314	2163789
7	Phenol, 2,6-dimethoxy-	154	Syringol lignin	11178985	13326663
8	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	164	Guaiacol lignin	5381775	7620069
9	Phenol, 4-methoxy-3-(methoxymethyl)-	168	Guaiacol lignin	6257983	4323071
10	Vanillin	152	Guaiacol lignin	2654063	1975985
11	Benzene, 1,2,3-trimethoxy-5-methyl-	182	Syringol lignin	1699993	1290719
12	3',5'-Dimethoxyacetophenone	180	Lignin	20521506	13421462
13	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	194	Syringol lignin	20801282	9249874
14	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	182	Syringol lignin	3075149	3025392
15	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	196	Syringol lignin	1191286	1670981

6.3.5 Combustion studies

6.3.5.1 Thermogravimetric Analysis (TGA)

Mass loss and DTG curves obtained from TGA char combustion plotted against temperature for the 2008 and 2011 samples are shown in Figures 6.17 and 6.18 respectively. The mass loss curves are represented using a solid line while the DTG curves are represented with a dashed line. On the mass loss curve, the large decrease in mass is due to char combustion and the final residue which remains is the ash.

On the DTG curves the peaks between 425 and 490^{o}C are attributed to char combustion. From Figures 6.17 and 6.18, it is seen that all the samples have similar char combustion peak temperatures except *S.elaeagnos Scop* which has lower char combustion peak temperature.

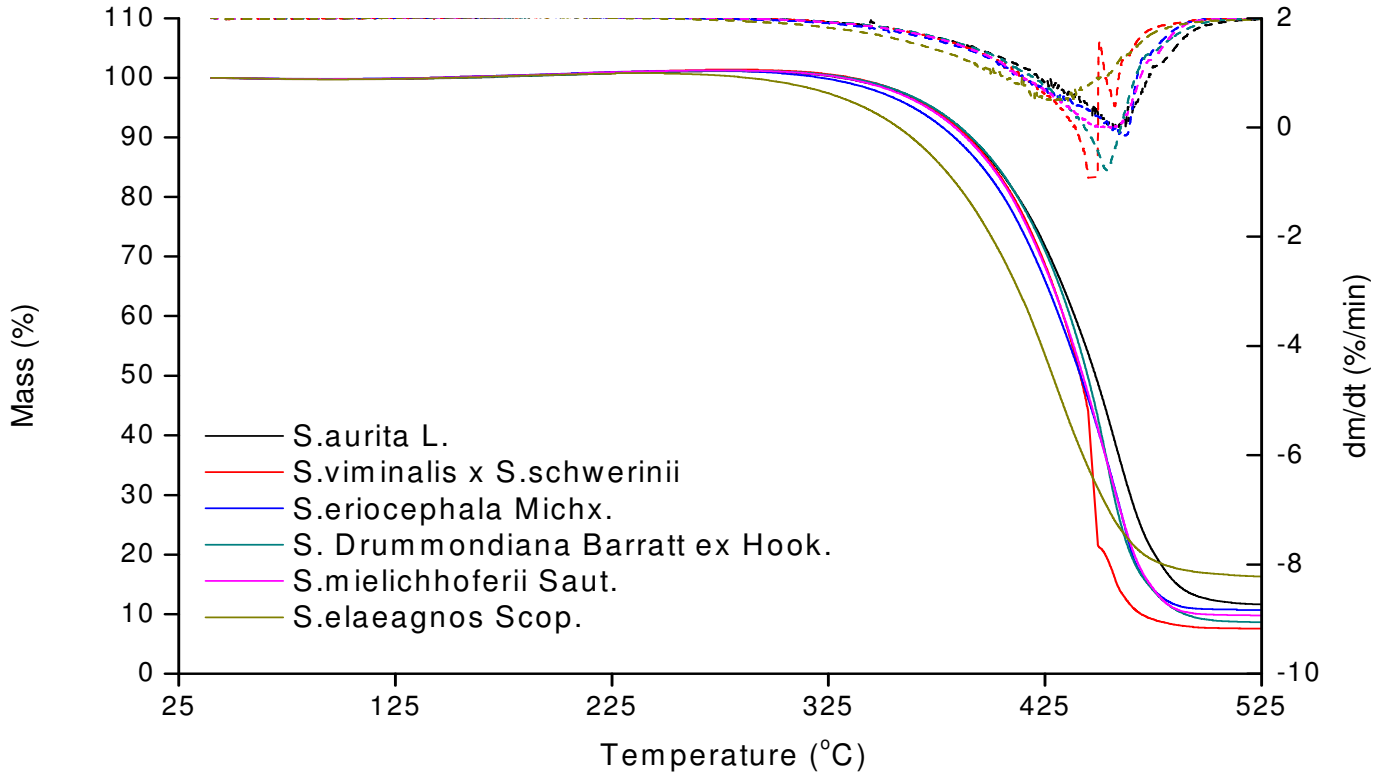


Figure 6 1 7 Mass loss curves and Derivative of mass loss (DTG) curves against temperature for the 2008 samples from TGA char combustion studies

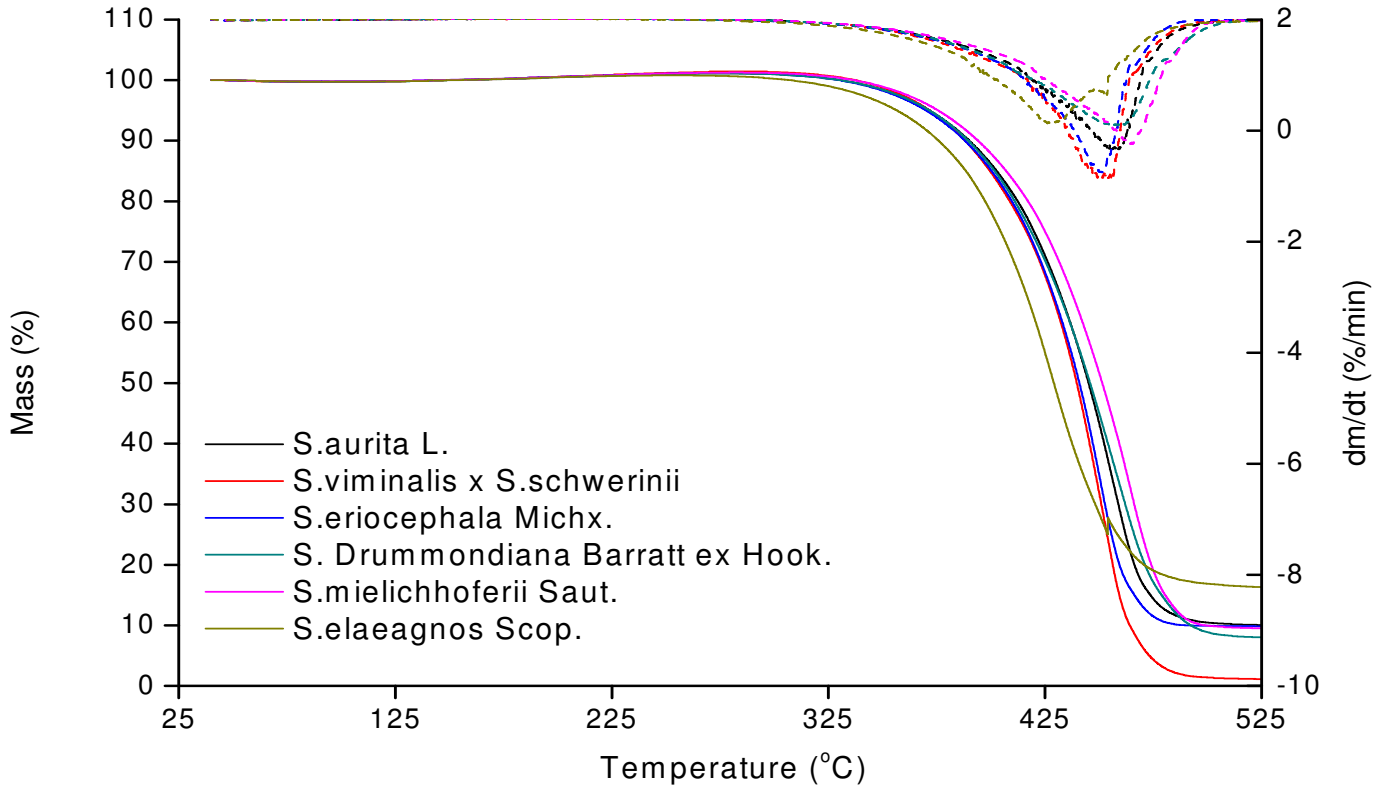


Figure 6 1 8 Mass loss curves and Derivative of mass loss (DTG) curves against temperature for the 2011 samples from TGA char combustion studies

The pyrolysis and char combustion peak temperatures for all the samples for both the years are reported in Table 6.8 along with the potassium (K) content of the fuels.

Table 6 8 K content, pyrolysis and char combustion peak temperatures for six genotypes for 2008 and 2011 samples

Genotype	K Content (ppm)		Temperature (^{o}C)			
			Volatile Release		Char Combustion	
	2008	2011	2008	2011	2008	2011
S.aurita L	2199	1713	360.6	362.8	462.3	458.5
S.viminalis x S.schwerinii	1953	1997	359.8	364.3	446.5	453.2
S.eriocephala Michx	1777	1737	359.5	364.7	461.5	451.6
S. drummondiana Barratt ex Hook	2241	2139	362.8	362.8	453.7	456.0
S.mielichhoferii Saut	2117	2078	362.3	364.5	456.5	464.2
S.elaeagnos Scop	5321	n.a	341.4	340.6	435.9	428.7

n.a. not analysed

The lower pyrolysis peak temperature of *S.elaeagnos Scop* could be a result of the catalytic effect of some inorganic metals. Previous studies have shown that metals like potassium (K), phosphorous (P) and iron (Fe) catalyse pyrolysis reactions and K, iron (Fe), calcium (Ca) and magnesium (Mg) catalyse char combustion but P inhibits char combustion (Fuentes et al., 2008). From Table 6.8 it can be seen that all the genotypes except *S.elaeagnos Scop* have similar potassium contents and pyrolysis and char combustion peak temperatures. *S.elaeagnos Scop* has a high K content and a low volatile release peak temperature indicating that K acts as a catalyst during the pyrolysis of SRC willow. For char combustion, *S.elaeagnos Scop* also has a lower peak temperature to that of all other genotypes. The effect of K content on char combustion needs to be further studied as the exact K content of the char needs to be known before any solid conclusions can be made this is because K is very volatile and some of it is given off as volatiles during the pyrolysis process, though most of it is retained in the char (Baxter et al., 1998).

6.3.5.2 Single Particle Combustion

The single particle combustion experiments were conducted according to Section 3.3.13 for the 2011 samples only since appropriate particle size was not available for the 2008 samples. Approximately 12 particles of 3mm length and 1-2mm diameter and similar shapes but different masses of each genotype were used for this experiment. An example of the particles is shown in Figure 6.19. The effect of particle mass and genotype on the duration of the devolatilisation and char combustion stages of the particles were investigated in this study.

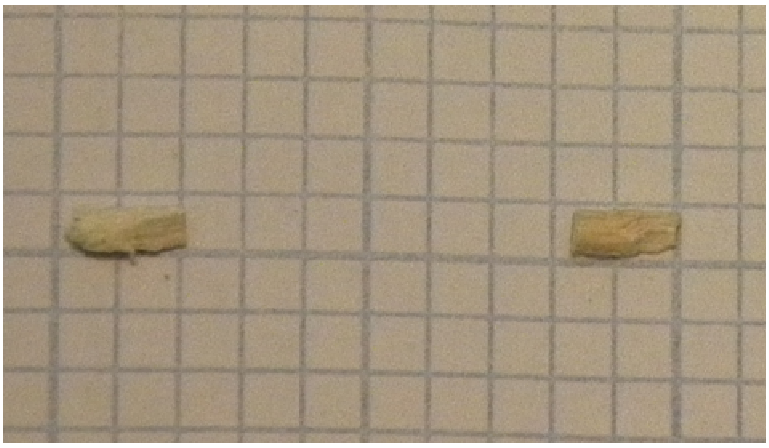
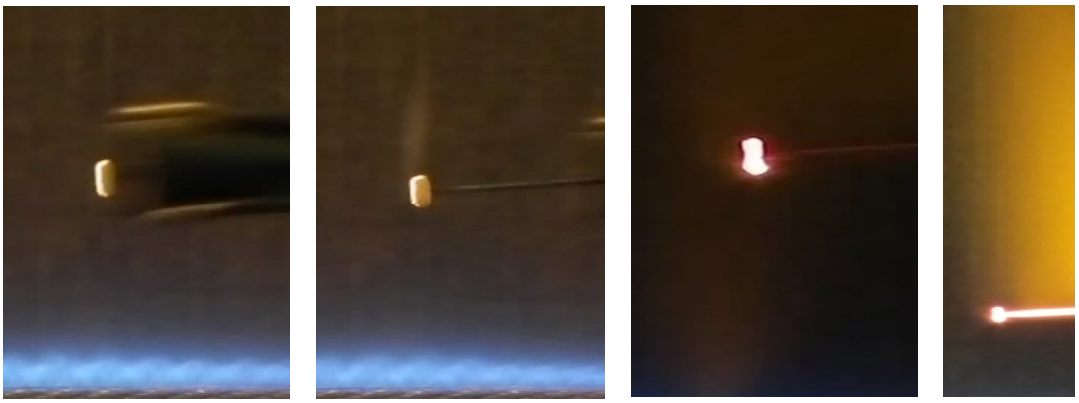


Figure 6 1 9 Particles for *S.mielichhoferii Saut* before burning

Four critical stages are taken into account. Firstly, the particle being exposed to the flame, followed by the ignition of the particle, then the beginning of char burnout, marked by the extinguishing of the volatile flame, and finally the end of char burnout when the particle shrinks. An example of these four stages is shown in Figure 6.20. The beginning of the particle ignition is marked by the dull white flame which indicates the evolution of moisture. Towards the end of volatile combustion, char combustion occurs simultaneously and can be seen by the glowing of the char particle at the bottom. Once the volatile flame terminates, the glowing char particle can be seen clearly as in Figure 6.20c. The char particle looks very similar to that of the original particle. During char combustion the particle slowly starts to shrink and the end of char combustion is marked by the particle shrinking rapidly.



(a)	**(b)**	**(c)**	**(d)**
(1.034 s)	*(1.101 s)*	*(2.602 s)*	*(5.138 s)*
Particle exposed	Particle Ignited	Volatile Flame Extinguished	Char Burnout Complete

Figure 6 2 0 The 4 critical stages taken into account for the single particle combustion experiments

The devolatalisation of the particles occurred within a range of approximately 1-3 seconds while char combustion occurred within a range of approximately 0.6-4 seconds. While calculating the duration of the devolatilisation and char combustion stages, some judgement is needed for the start and end of these two processes, and these may be taken at different times by different individuals. Figures 6.21 and 6.22 show the duration of the volatile flame and char combustion respectively plotted against particle mass for the particles of all six genotypes.

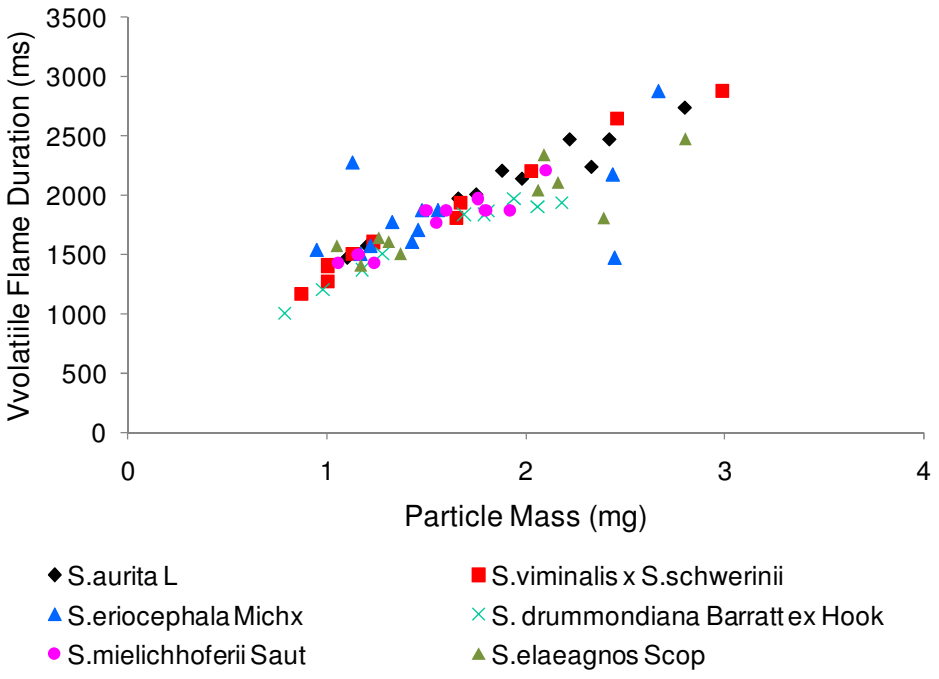


Figure 6 2 1 Volatile Flame Duration against Particle Mass of particles for the six genotypes

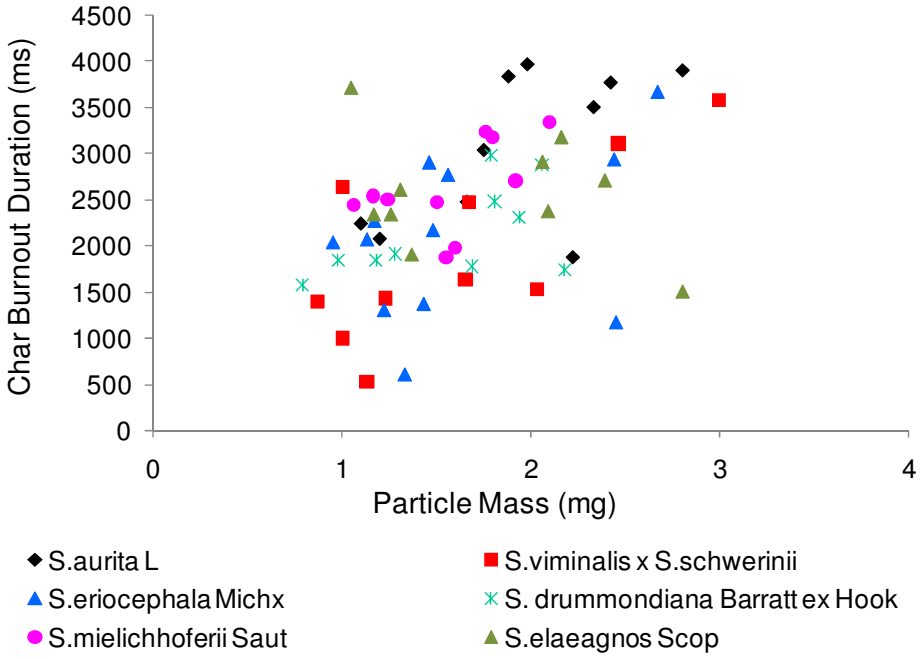


Figure 6 2 2 Char Combustion Duration against Particle Mass of particles for the six genotypes

For the duration of the volatile flame, all the genotypes follow a similar trend as shown in Figure 6.19. Heavier particles have a longer volatile flame duration compared to the lighter particles. The correlation (R^2) values for the volatile combustion and char combustion durations with particle mass are listed in Table 6.9.

Table 6 9 Correlation of Volatile Flame and Char Combustion Duration (ms) with Particle Mass (mg)

Genotype	Correlation of Time (ms) with Particle Mass (mg)	
	Volatile Flame (R^2)	Char Combustion (R^2)
S.aurita L	0.9505	0.9847
S.viminalis x S.schwerinii	0.9836	0.5369
S.eriocephala Michx	0.2801	0.1612
S. drummondiana Barratt ex Hook	0.9453	0.3144
S.mielichhoferii Saut	0.8720	0.2897
S.elaeagnos Scop	0.7576	0.0963

For char burnout, there is a larger scatter in the results since it is very difficult to see exactly when the particle starts to shrink and mark the exact end point of char combustion. Hence the points on the graph (Figure 6.22) are more scattered and the particular trends cannot be seen very clearly, although the char burnout duration for most of the samples seems to be increasing with increasing particle mass.

6.4 Conclusion

It is found that the samples selected for this study follow the same biochemical composition trends for 2008 and 2011 except in the case of hemicellulose. The cellulose and lignin contents of the 2011 samples are lower than those of the 2008 samples. Cellulose contents are in the range of 33-55 and 38-48% respectively for the 2008 and 2011 samples respectively while the lignin contents lie in the range of 15-23 and 14-19% respectively. The ash composition also follow similar trends for both years except

for CaO. The 2011 samples have lower ash components compared to the 2008 samples. These lower biochemical and ash components in the 2011 samples could be a result of aging or overwintering since the 2008 and 2011 samples were taken in December and February respectively.

Ash behaviour has been explored by calculating a number of characteristic indices and also by the application of two experimental tests; ash fusion tests and STA-MS. All the genotypes have low slagging tendencies except *S.elaeagnos Scop* since $R_{b/a}$ is >1. The ash of the 5 genotypes tested melts at temperatures >1500^{o}C which is a desirable fuel property since there are lower chances of boilers and furnaces corroding. The major products detected during ash melting in the STA-MS are CO_2 from $CaCO_3$ and SO_2 from $CaSO_4$ and HCl for some genotypes.

Grindability tests show *S.elaeagnos Scop* to be remarkably different to the other genotypes. It breaks down more easily to desirable particle size for co-firing compared to other genotypes.

Some pyrolysis products are highly sensitive to the hemicelluloses and lignin contents in the fuels as seen from the Py GC-MS tests.

From the TGA combustion it is seen that *S.elaeagnos Scop* has much lower pyrolysis and char combustion peak but a higher K content compared to the other genotypes indicating that K catalyses these reactions. From the single particle burning experiments the volatile flame duration was approximately 1-3 seconds while the char combustion duration was el p 0.6-4 seconds. A similar trend is observed for all the genotypes for the volatile flame duration but no particular trends are observed for the char combustion duration since the points are more scattered.

In summary, all the genotypes except *S.elaeagnos Scop* exhibit very similar fuel properties. This particular genotype has a desirable trait (ease of grinding) that is worthy of further investigation.

Chapter 7

Conclusions and Future Work

7.1 Conclusions

Power station Fuels: Six different residues, Palm Kernel Expellers (PKE), Olive Residues A, B and C, Shea residue and Dried Distillers Grains and Solubles (DDGS) were studied for some of their combustion properties. It is found that all the residues have very high N contents especially DDGS which has an N content of almost 2-4 times that of all the other residues. Olive Residue C has the highest ash content and lowest calorific value. All the residues have a high tendency of slagging and fouling which can be detrimental in boilers and furnaces due to the loss of efficiency.

Pyrolysis studies revealed that some of these residues are very oily and a distinct decomposition peak is seen for this oil evaporation/decomposition reaction occurring at lower temperatures. PKE is seen to be the most reactive while Olive Residue C is the least reactive. DDGS has more hemicelluloses compared to cellulose as seen from the DTG curve, since it is more difficult to ferment but easier to hydrolyse. Py GC-MS products detected for all the residues at 600^{o}C are lignocelluloses including methoxyphenols and furfural derivatives, but for DDGS some hetrocyclic aromatics (also seen in amino acid pyrolysis) were also detected. For DDGS pyrolysed at 250^{o}C, furfural derivatives and some long chain fatty acids and esters were detected.

Kinetics of char combustion revealed that the char of Olive Residue B is the least reactive while that of PKE is the most reactive. Nitrogen partitioning of the fuels concluded that approximately 79-91% of the fuel nitrogen is evolved with volatiles and for DDGS, approximately 94% sulphur is evolved with volatiles. All the chars except for DDGS are depleted in nitrogen and DDGS is depleted in sulphur as seen from the C/N and C/S ratios respectively. The major N species detected during char combustion are NO and N_2^{2+} and small amounts of HCN are seen in the case of PKE, Olive Residue B and DDGS. C_2N_2 is also detected from PKE and DDGS and some HCNO is detected from the latter. SO_2 and SO are the major S species detected. Most of the N species are

detected later in combustion but in the case of DDGS where two types of chars are present, S species are detected early in combustion.

SRC willow Fertilizer Experiment: A field trial led by Rothamsted Research as part of the Supergen Bioenergy Consortium (www.supergen.bioenergy.net) investigated the fuel properties of SRC willow grown under 6 different fertilizer regimes and sampled in Oct-07, Mar-08, Sep-08, Mar-09, Oct-09 and Jan-10 (ie twice a year for three years) were characterised for their proximate, ultimate and ash compositions and the corresponding ash behaviour in terms of slagging and fouling. Some combustion tests were also conducted and regression analysis were carried out to understand the influence of some metals on volatile combustion peak temperature. The effect of application of different fertilizer treatments on the crop and sampling times of the year did influence the fuel properties of the crop. Also different parts of the crop (eg leaves and stems) exhibited different compositions and fuel properties.

Leaves and stems: The leaves of SRC willow have higher nitrogen and ash contents compared to the stems. Ash components like CaO, K_2O and P_2O_5 are higher in the stems compared to leaves. The alkali index of leaves is much higher than that of stems, while the $R_{b/a}$ is high for both leaves and stems.

Sampling Time: A general decrease in C content of SRC willow is seen over the sampling time. This in turn influences the CV which also decreases over the sampling time since it is highly dependant on the C content. The nitrogen content for SRC willow leaves generally decreases over sampling time although the Sep-08 sample in this case has the highest nitrogen content for all 4 treatment effects. The weight % CaO increases and wt % K_2O decrease in the leaves of SRC willow over the sampling time. For CaO this is not true for two treatments. The alkali index for both the leaves and stems decreases over the three year growth period as well as the annual growing season.

Treatment:. Nitrogen content in the fuel is not only influenced by the addition of nitrogen fertilizer but also the addition of K and S as fertilizers. Fertilizer treatment usually does not influence the ash content of the fuel, but, from this dataset, although limited, the application of sewage pellets as fertilizer may result in low ash.

Some fertilizer treatments do have a positive influence on fuel properties (eg addition of K and N can increase C content and CV of the fuel). Larger datasets are required to make firm conclusions and projections regarding the benefit of treatment response. The best time to harvest the willow would be in the spring when the leaves have fallen since it improves the fuel quality and also helps to recycle the nutrients to the soil from the leaf litter.

All these properties are not necessarily desirable in power stations. High N contents can lead to high NO_x emissions, while high K_2O in the ash can react with silica and sulphur to form silicates which lower ash melting temperatures. High alkali index and $R_{b/a}$ pose a tendency to cause fouling and slagging respectively in boilers and furnaces, hence lowering power plant efficiency. However, high CaO contents in the fuel are highly desirable since they increase the ash melting temperatures.

TGA Combustion Studies: From the TGA combustion studies, it was seen that leaves have a lower volatile combustion peak temperature compared to stems. It was also seen that as Ca, P and Mg contents in the fuell increase, the volatile combustion peak temperature also increases. Leaves show a strong positive correlation with total metals and volatile combustion peak temperature while stems show a weak negative correlation. This may imply that the metals in the leaves are more mobile compared to those in the stems.

SRC Willow Genetics: Six different genotypes harvested for 2 years (2008 and 2011) with high and low cellulose, hemicelluloses and lignin contents) were characterised for some of their fuel properties. *S aurita L, S Drummondiana Barratt ex Hook* and *S viminalis x S Schwerinii* have the lowest hemicelluloses, cellulose and lignin contents respectively, while *S.mielichhoferii Saut, S.eriocephala Michx* and *S.elaeagnos Scop* have the highest hemicellulose, cellulose and lignin contents respectively

The biochemical composition of the different genotypes followed the same trend for both the years but the 2011 samples had lower amounts of biochemical components

compared to 2008. Similarly the components in the ash except for CaO also followed similar trends for the two years with 2008 samples having higher ash components compared to the 2011 samples. The lower biochemical and ash components in the 2011 samples could be due to overwintering since the 2008 and 2011 samples were harvested in December and February respectively, or due to change in composition over the years.

Slagging and fouling indices were calculated for the samples and ash fusion and ash melting tests were conducted. All the genotypes have low tendencies of slagging and fouling except *S.elaeagnos Scop* (highest lignin content) since $R_{b/a}$ is >1. Ash fusion tests exhibit that the ashes of the 5 genotypes tested melt at temperatures >1500^{o}C which is a desirable trait, since there are lower tendencies of slagging and fouling to occur. The major products detected during ash melting in the STA-MS are CO_2 from $CaCO_3$ and SO_2 from $CaSO_4$ and HCl for some genotypes.

Grindability tests show *S.elaeagnos Scop* to be remarkably different to the other genotypes. It breaks down more easily to desirable particle size for co-firing compared to other genotypes. This is a highly desirable quality in power stations since less energy would be required in the size reduction of biomass.

Some pyrolysis products are highly sensitive to the hemicellulose and lignin contents but not very sensitive to the cellulose contents as illustrated from the Py GC-MS results.

During pyrolysis and combustion studies, the volatile combustion peak (maximum rate of volatile combustion) and char combustion peak (maximum rate char combustion) temperatures were lower for the *S.elaeagnos Scop* while its potassium content was much higher compared to the other fuels. This indicates that K catalyses the reactions. Single particle burning experiments showed that the volatile flame duration was approximately 1-3 seconds while the char combustion duration was 0.6-4 seconds.

In summary, all the genotypes except *S.elaeagnos Scop* exhibit very similar fuel properties. This particular genotype has a desirable trait (ease of grinding) that is worthy of further investigation.

7.2 Future Work

1. **Extending fertilizer application dataset** While the work in this thesis demonstrates some significant variation in fuel properties with agronomy, there is a natural scatter on the data that is difficult to interpret over the three years studied here .A larger dataset for the fertilizer application experiment would give added confidence to the impact of agronomy on fuel properties. This coupled with data on yield and lifecycle Greenhouse Gas emissions will give further insight into agronomic best practice for SRC willow in the UK.
2. **Extending genetic data:** The work presented here demonstrated some of the fuel properties of a small subset of genotypes One of the genotypes exhibits some very interesting properties especially the ease with which its particle size can be reduced (grindability). A larger variety of genotypes would help map out the yield and GHG emissions as well as fuel properties which could assist farmers in breeding genotypes to produce fuels with high yields, low GHG emissions and optimum fuel properties.
3. **Catalytic effect of metals on char combustion:** An investigation on the effect of metal content on the volatile combustion has already been carried out in this thesis and showed some interesting results like the catalytic effect of certain metals on the volatile combustion peak temperature. However, it would be interesting to carry out a similar investigation for the char combustion. In order to do this, the metals in the char would need to be quantified before carrying out a regression analysis.

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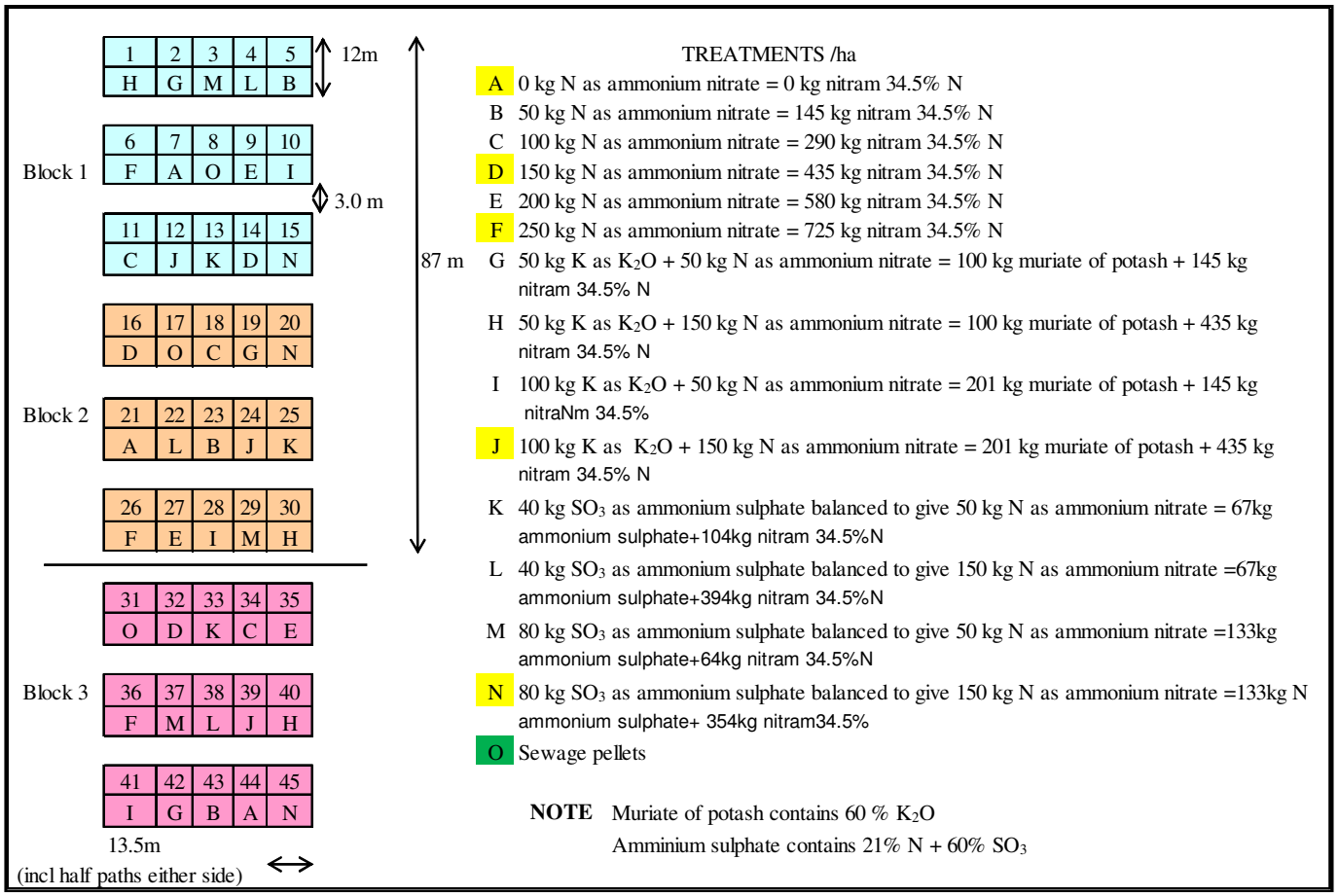
APPENDIX A: SRC Willow Fertilizer Experiment Field Trial

SRC willow block and treatment layout and Treatment details



APPENDIX B: Fuel Characteristics and Combustion Peak Temperature

Table B1 Fuel characteristics and Combustion peak temperatures for Treatment A (0Kg N)

		dry basos (db)									(°C)	
Sampling	**Plot**	**C**	**H**	**N**	**O**	**Moisture**	**Ash**	**CV (ols) (kJ/kg)**	**CV (pls) (kJ/kg)**	**CV (MJ/kg)**	**T_{vm}**	**T_{char}**
1st leaves	7	50.08	6.55	1.97	41.41	7.26	5.87	20333.04	20277.15	20.328	312.9	446.4
15/10/2007	21	50.39	6.75	1.91	40.95	7.23	6.26	20551.43	20474.56	20.537	331.5	444.0
	44	50.20	6.57	1.76	41.47	6.43	6.12	20372.83	20313.08	20.366	321.4	453.1
Average		50.22	6.62	1.88	41.27	6.97	6.08	20419.10	20354.93	20.410	321.9	447.8
Std dev		0.16	0.11	0.11	0.28	0.47	0.20	116.31	105.15	0.11	9.3	4.7
3rd leaves	7	49.01	6.53	2.65	41.81	5.34	7.27	19925.17	19881.58	19.926	339.5	462.0
30/09/2008	21	50.27	6.89	2.43	40.42	4.87	7.37	20612.22	20525.53	20.593	350.2	460.9
	44	49.22	6.77	2.75	41.26	5.73	7.23	20111.46	20049.91	20.104	316.7	464.1
Average		49.50	6.73	2.61	41.17	5.31	7.29	20216.28	20152.34	20.208	335.4	462.3
Std dev		0.67	0.18	0.16	0.70	0.43	0.07	355.32	333.97	0.35	17.1	1.6
5th leaves	7	49.55	6.29	2.21	41.95	7.36	8.32	20034.80	20002.19	20.041	315.5	464.9
12/10/2009	21	48.47	6.03	1.65	43.85	6.31	8.65	19415.94	19399.46	19.429	327.2	467.5
	44	48.96	6.23	2.48	42.33	7.03	7.97	19791.78	19766.33	19.801	326.1	481.6
Average		48.99	6.18	2.12	42.71	6.90	8.31	19747.50	19722.66	19.757	322.9	471.3
Std dev		0.54	0.14	0.42	1.01	0.54	0.34	311.79	303.73	0.31	6.5	9.0
1st stems	7	50.58	6.16	0.16	43.09	5.48	2.24	20178.38	20152.59	20.187	341.4	464.4
15/10/2007	21	51.04	6.44	0.00	42.52	5.48	2.25	20477.78	20424.63	20.474	344.3	461.1
	44	50.58	6.16	0.00	43.27	5.29	0.79	20151.65	20125.85	20.160	345.9	478.0
Average		50.73	6.25	0.05	42.96	5.42	1.76	20269.27	20234.36	20.27	343.9	467.8
Std dev		0.26	0.16	0.09	0.39	0.11	0.30	181.07	165.32	0.17	2.3	8.9
2nd stems	7	50.91	6.21	0.09	42.79	4.74	1.97	20334.15	20306.26	20.342	341.3	467.0
11/03/2008	21	51.67	6.10	0.00	42.23	5.27	2.13	20605.69	20601.32	20.625	342.0	455.7
	44	52.27	6.35	0.17	41.21	4.37	0.89	21020.22	20992.39	21.029	343.0	475.1
Average		51.62	6.22	0.09	42.07	4.79	0.89	20653.35	20633.32	20.665	342.1	465.9
Std dev		0.68	0.12	0.09	0.80	0.45	0.34	345.51	344.18	0.35	0.9	9.8
3rd stems	7	49.05	5.98	0.41	44.56	5.11	0.96	19483.58	19465.40	19.495	339.2	456.4
30/09/2008	21	49.03	5.97	0.33	44.67	4.93	0.71	18451.84	19445.29	19.475	345.1	458.4
	44	48.62	6.12	0.32	44.93	5.02	0.88	18292.85	19307.63	19.343	339.9	456.8
Average		48.90	6.02	0.36	44.72	5.02	1.26	18742.76	19406.10	19.438	341.4	457.2
Std dev		0.24	0.09	0.05	0.19	0.09	0.07	646.48	85.88	0.08	3.2	1.1
4th stems	7	48.32	5.98	0.39	45.32	2.42	1.30	19175.52	19156.72	19.187	347.1	458.0
08/12/2003	21	47.09	5.89	0.43	46.59	2.05	1.43	18248.96	18642.34	18.668	346.0	462.6
	44	48.72	5.78	0.52	44.98	4.63	1.29	18382.09	19294.48	19.319	346.5	467.2
Average		48.04	5.89	0.44	45.63	3.03	1.41	18602.19	19031.18	19.058	346.5	462.6
Std dev		0.28	0.14	0.09	0.85	1.56	0.16	561.04	97.42	0.09	0.5	4.6
5th stems	7	49.63	6.07	0.26	44.04	6.59	0.90	19742.39	19719.18	19.752	346.8	466.3
12/10/2009	21	45.94	5.58	0.28	48.20	6.47	1.27	17035.82	18132.57	18.153	348.8	468.1
	44	49.29	6.13	0.41	44.17	6.66	1.19	18189.53	19608.22	19.644	346.1	479.6
Average		48.29	5.93	0.31	45.47	6.57	1.12	18322.58	19153.32	19.18	347.3	471.3
Std dev		0.24	0.04	0.11	2.36	0.05	0.21	1098.04	78.47	0.08	1.4	7.2
6th stems	7	50.01	5.76	0.28	43.95	6.09	1.09	19791.44	19797.64	19.815	343.3	462.20.
18/01/2010	21	49.54	5.71	0.21	44.53	6.44	1.18	18291.84	19579.45	19.598	362.1	480.2
	44	49.20	5.66	0.32	44.81	6.47	0.97	18172.95	19440.73	19.459	346.5	467.2
Average		49.58	5.71	0.27	44.43	6.33	1.08	18752.07	19605.94	19.62	350.6	473.7
Std dev		0.57	0.07	0.03	0.44	0.27	0.08	1144.44	252.37	0.25	10.0	9.2

Table B2 Fuel characteristics and Combustion peak temperatures for Treatment D (150Kg N)

		dry basos (db)									(°C)	
Sampling	**Plot**	**C**	**H**	**N**	**O**	**Moisture**	**Ash**	**CV (ols) (kJ/kg)**	**CV (pls) (kJ/kg)**	**CV (MJ/kg)**	**T_{vm}**	**T_{char}**
1st leaves	14	49.32	6.76	2.17	41.76	5.86	6.71	20079.83	20015.25	20.071	305.9	440.9
15/10/2007	16	49.51	6.75	1.93	41.80	6.23	6.45	20139.30	20071.42	20.129	320.1	446.7
	32	50.96	6.95	2.10	39.99	7.05	6.31	20934.21	20832.48	20.908	316.6	438.4
Average		49.93	6.82	2.07	41.18	6.25	6.49	20384.45	20306.38	20.369	314.2	442.0
Std dev		0.90	0.11	0.12	1.03	0.23	0.20	477.04	456.48	0.47	7.4	4.3
3rd leaves	14	48.77	6.30	2.34	42.59	4.81	7.09	19709.76	19680.43	19.717	307.5	456.8
30/09/2008	16	49.08	6.35	2.54	42.02	5.22	7.56	19890.23	19856.69	19.896	330.6	446.4
	32	50.98	6.75	2.69	39.58	5.63	6.94	20932.78	20855.61	20.918	320.6	445.3
Average		49.61	6.47	2.53	41.40	5.22	7.20	20177.59	20130.91	20.177	319.6	449.5
Std dev		1.20	0.25	0.18	1.60	0.41	0.32	660.21	633.77	0.65	11.6	6.3
5th leaves	14	46.78	5.69	1.40	46.12	6.70	8.26	18622.44	18620.24	18.641	325.3	461.5
12/10/2009	16	48.21	6.12	1.98	43.70	6.63	8.68	19369.26	19351.35	19.382	332.6	464.5
	32	49.57	6.18	1.76	42.50	6.79	7.95	19945.78	19919.97	19.955	327.7	453.7
Average		48.19	6.00	1.71	44.10	6.71	8.30	19312.49	19297.19	19.33	328.6	459.9
Std dev		1.39	0.27	0.29	1.85	0.08	0.36	663.50	651.56	0.66	3.7	5.6
1st stems	14	47.04	6.06	0.00	46.90	4.11	0.89	18610.17	18596.70	18.625	336.72	449.15
15/10/2007	16	49.28	6.46	0.00	44.26	3.59	1.04	19685.71	19633.31	19.682	340.27	472.90
	32	49.40	6.58	0.21	43.81	5.81	0.71	19807.86	19746.77	19.800	337.45	472.94
Average		48.57	6.37	0.07	44.99	4.50	0.78	19367.91	19325.59	19.369	338.1	465.0
Std dev		1.33	0.27	0.12	1.67	1.16	0.30	659.06	633.78	0.65	1.9	13.7
2nd stems	14	49.83	6.34	0.00	43.83	4.23	2.43	19890.08	19844.71	19.890	343.42	486.38
11/03/2008	16	49.78	6.39	0.20	43.63	4.95	1.11	19913.59	19865.15	19.912	338.86	465.59
	32	50.49	6.59	0.40	42.52	5.31	0.69	20340.08	20272.19	20.329	344.64	472.26
Average		50.03	6.44	0.20	43.33	4.83	0.89	20047.91	19994.02	20.043	342.3	474.7
Std dev		0.40	0.13	0.20	0.71	0.55	0.34	253.29	241.12	0.25	3.0	10.6
3rd stems	14	50.30	6.45	0.35	42.90	5.15	1.11	20191.01	20136.58	20.186	341.44	452.30
30/09/2008	16	49.87	6.41	0.40	43.33	6.59	0.54	19985.29	19935.25	19.983	340.72	466.40
	32	48.71	6.39	0.38	44.52	5.07	1.12	19457.97	19416.23	19.459	342.52	456.06
Average		49.63	6.42	0.37	43.58	5.60	1.26	19878.09	19829.35	19.876	341.6	458.3
Std dev		0.82	0.03	0.02	0.84	0.86	0.07	378.10	371.66	0.37	0.9	7.3
4th stems	14	48.33	6.06	0.34	45.27	1.89	1.22	19198.03	19175.10	19.208	342.83	452.26
08/12/2003	16	47.86	5.99	0.40	45.75	2.95	1.39	18988.87	18971.42	19.001	345.22	458.11
	32	48.54	6.13	0.36	44.97	2.75	1.26	19308.47	19281.73	19.317	345.09	462.11
Average		48.25	6.06	0.37	45.33	2.53	1.41	19165.12	19142.75	19.175	344.4	457.5
Std dev		0.15	0.05	0.02	0.40	0.61	0.16	78.09	75.39	0.08	1.3	5.0
5th stems	14	47.23	5.75	0.22	46.79	6.33	0.78	18658.16	18648.61	18.674	346.39	461.86
12/10/2009	16	48.76	5.98	0.40	44.87	6.33	1.17	19360.00	19341.02	19.371	346.93	455.64
	32	48.83	5.96	0.28	44.94	6.18	1.11	19368.75	19350.55	19.381	349.27	460.00
Average		48.27	5.90	0.30	45.53	6.28	1.02	19128.97	19113.39	19.14	347.5	459.2
Std dev		0.90	0.12	0.09	1.09	0.09	0.21	407.76	402.54	0.41	1.5	3.2
6th stems	14	45.07	5.50	0.28	49.16	5.96	0.82	17794.53	17799.02	17.816	344.59	452.99
18/01/2010	16	49.05	6.04	0.18	44.73	5.94	0.94	19476.08	19453.03	19.486	346.93	469.91
	32	48.45	6.24	0.22	45.08	5.66	1.21	19282.25	19249.86	19.288	343.42	460.16
Average		47.52	5.93	0.23	46.32	5.85	0.99	18850.95	18833.97	18.86	345.0	461.0
Std dev		2.15	0.39	0.05	2.46	0.17	0.20	920.01	902.03	0.91	1.8	8.5

Table B3 Fuel characteristics and Combustion peak temperatures for Treatment F (250Kg N)

		dry basos (db)									(°C)	
Sampling	**Plot**	**C**	**H**	**N**	**O**	**Moisture**	**Ash**	**CV (ols) (kJ/kg)**	**CV (pls) (kJ/kg)**	**CV (MJ/kg)**	T_{vm}	T_{char}
1st leaves	6	51.11	7.03	2.49	39.37	7.38	5.41	21093.18	20982.76	21.063	310.64	448.81
15/10/2007	26	49.35	6.68	1.72	42.25	7.95	6.56	20012.91	19951.32	20.006	316.29	450.42
	36	49.49	6.80	1.90	41.81	7.39	6.84	20139.99	20068.50	20.128	311.94	437.91
Average		49.98	6.84	2.04	41.14	7.57	6.27	20415.36	20334.19	20.399	313.0	445.7
Std dev		0.98	0.18	0.41	1.55	0.33	0.76	590.44	564.72	0.58	3.0	6.8
3rd leaves	6	48.75	6.57	3.20	41.48	5.85	8.95	19892.78	19851.89	19.895	337.36	457.77
30/09/2008	26	48.44	6.16	2.26	43.14	5.82	8.06	19516.54	19496.46	19.528	331.36	467.62
	36	49.72	6.55	2.43	41.30	5.83	7.37	20230.35	20177.75	20.227	327.71	454.01
Average		48.97	6.43	2.63	41.97	5.83	8.13	19879.89	19842.03	19.883	332.1	459.8
Std dev		0.67	0.23	0.50	1.02	0.02	0.79	357.08	340.75	0.35	4.9	7.0
5th leaves	6	48.82	6.38	2.52	42.27	7.25	8.68	19780.15	19746.61	19.786	323.76	457.09
12/10/2009	26	48.52	6.05	1.82	43.60	6.17	7.31	19467.41	19450.35	19.480	327.15	451.36
	36	49.60	6.14	1.86	42.40	6.35	6.74	19959.66	19937.35	19.970	332.09	456.83
Average		48.98	6.19	2.07	42.76	6.59	7.58	19735.74	19711.44	19.745	327.7	455.1
Std dev		0.56	0.17	0.39	0.73	0.58	1.00	249.11	245.40	0.25	4.2	3.2
1st stems	6	50.53	6.54	0.00	42.94	5.79	0.92	20283.57	20219.13	20.274	336.36	468.72
15/10/2007	26	50.23	6.68	0.16	42.93	5.75	1.16	20222.93	20146.28	20.208	343.33	466.86
	36	47.92	6.32	0.25	45.51	5.67	1.25	19071.40	19041.64	19.079	342.07	483.27
Average		49.56	6.51	0.14	43.79	5.74	0.78	19859.30	19802.35	19.854	340.6	473.0
Std dev		1.43	0.18	0.13	1.49	0.06	0.30	683.01	659.80	0.67	3.7	9.0
2nd stems	6	48.49	4.48	0.00	47.03	5.19	0.69	18786.92	18839.41	18.829	340.32	473.02
11/03/2008	26	48.89	6.39	0.22	44.49	5.06	0.66	19519.74	19475.72	19.520	343.51	478.19
	36	49.04	6.25	0.00	44.70	4.82	0.96	19514.27	19477.10	19.518	344.32	474.83
Average		48.81	5.71	0.07	45.41	5.02	0.89	19273.64	19264.08	19.289	342.7	475.3
Std dev		0.29	1.06	0.13	1.41	0.19	0.34	421.52	367.78	0.40	2.1	2.6
3rd stems	6	50.15	6.47	0.58	42.80	5.55	1.40	20160.67	20105.81	20.156	340.49	457.60
30/09/2008	26	48.60	6.38	0.38	44.65	5.12	1.28	19403.37	19363.68	19.406	331.02	431.20
	36	46.86	6.01	0.32	46.81	5.15	1.26	18567.27	18557.82	18.584	343.33	458.16
Average		48.54	6.28	0.43	44.75	5.27	1.26	19377.11	19342.44	19.382	338.3	449.0
Std dev		1.65	0.24	0.14	2.01	0.24	0.07	797.02	774.21	0.79	6.4	15.4
4th stems	6	48.11	5.97	0.42	45.50	2.27	1.27	19090.30	19072.67	19.102	344.57	464.18
08/12/2003	26	48.58	6.59	0.38	44.45	3.60	1.30	19454.16	19403.90	19.452	344.46	454.95
	36	48.36	6.52	0.43	44.68	2.65	1.43	19343.84	19300.24	19.345	338.52	438.00
Average		48.35	6.36	0.41	44.88	2.84	1.41	19296.10	19258.94	19.300	342.5	452.4
Std dev		0.18	0.39	0.01	0.55	0.27	0.16	179.28	160.91	0.17	3.5	13.3
5th stems	6	49.54	6.11	0.88	43.47	5.63	1.04	19798.49	19774.05	19.808	345.76	461.10
12/10/2009	26	48.79	6.08	0.78	44.36	5.88	0.97	19451.70	19428.69	19.461	349.00	473.90
	36	48.75	6.02	0.34	44.90	5.92	0.70	19359.44	19338.14	19.370	350.89	459.05
Average		49.02	6.07	0.67	44.24	5.81	0.90	19536.54	19513.63	19.55	348.6	464.7
Std dev		0.56	0.07	0.38	0.72	0.21	0.24	310.45	308.23	0.31	2.6	8.0
6th stems	6	48.22	6.01	0.27	45.51	5.80	0.87	19124.97	19104.64	19.136	343.24	462.54
18/01/2010	26	49.01	5.89	0.37	44.72	5.68	1.06	19439.55	19426.15	19.453	345.04	454.18
	36	48.34	5.98	0.34	45.35	5.68	0.91	19176.81	19157.72	19.188	345.13	453.50
Average		48.52	5.96	0.33	45.19	5.72	0.95	19247.11	19229.50	19.26	344.5	456.7
Std dev		0.08	0.02	0.05	0.42	0.08	0.03	36.66	37.54	0.04	1.1	5.0

Table B4 Fuel characteristics and Combustion peak temperatures for Treatment J (150Kg N + 100Kg K)

		dry basos (db)									(°C)	
Sampling	**Plot**	**C**	**H**	**N**	**O**	**Moisture**	**Ash**	**CV (ols) (kJ/kg)**	**CV (pls) (kJ/kg)**	**CV (both) (MJ/kg)**	T_{vm}	T_{char}
1st leaves	12	50.14	6.23	2.51	41.13	6.84	5.87	20,310	20,285	20.319	302.7	437.7
15/10/2007	24	48.31	5.77	1.88	44.04	7.10	6.26	19,310	19,307	19.329	310.6	443.8
	39	49.32	5.90	2.30	42.47	7.12	6.12	19,819	19,814	19.837	311.9	442.5
Average		49.26	5.97	2.23	42.55	7.02	6.08	19,813	19,802	19.828	308.4	441.3
Std dev		0.92	0.23	0.32	1.46	0.16	0.20	500	489	0.50	5.0	3.2
3rd leaves	12	50.33	6.94	3.44	39.29	5.97	7.27	20,795	20,706	20.775	312.4	486.4
30/09/2008	24	50.12	6.47	2.64	40.77	5.95	7.37	20,410	20,363	20.409	315.6	449.3
	39	51.48	7.18	3.06	38.29	5.63	7.23	21,418	21,287	21.378	319.1	453.8
Average		50.64	6.86	3.05	39.45	5.85	7.29	20,874	20,786	20.854	315.7	463.2
Std dev		0.73	0.36	0.40	1.25	0.19	0.07	508	467	0.49	3.3	20.3
5th leaves	12	50.20	6.26	1.91	41.63	6.75	8.10	20,273	20,243	20.280	328.5	458.0
12/10/2009	24	49.97	6.35	2.07	41.62	7.04	7.92	20,222	20,184	20.226	330.2	462.5
	39	52.20	6.77	2.86	38.18	7.22	8.09	21,548	21,469	21.532	335.5	468.7
Average		50.79	6.46	2.28	40.48	7.00	8.04	20,681	20,632	20.679	331.4	463.1
Std dev		1.23	0.27	0.51	1.99	0.24	0.10	751	726	0.74	3.6	5.4
1st stems	12	48.03	5.41	0.44	46.11	5.63	0.91	18,925	18,928	18.945	335.2	455.7
15/10/2007	24	47.58	5.13	0.47	46.82	5.56	1.00	18,694	18,701	18.716	336.3	459.1
	39	48.28	5.35	0.58	45.80	5.94	0.89	19,018	19,028	19.042	337.1	460.5
Average		47.96	5.29	0.50	46.25	5.71	0.78	18,879	18,886	18.901	336.2	458.5
Std dev		0.36	0.15	0.07	0.52	0.20	0.30	167	167	0.17	0.9	2.5
2nd stems	12	46.98	5.06	0.48	47.47	4.85	0.50	18,469	18,469	18.487	342.7	464.4
11/03/2008	24	48.51	5.47	0.52	45.51	5.09	1.08	19,132	19,138	19.154	342.4	473.9
	39	47.31	5.11	0.41	47.17	5.17	1.09	18,586	18,590	18.606	342.3	466.2
Average		47.60	5.22	0.47	46.72	5.04	0.89	18,729	18,732	18.749	342.5	468.2
Std dev		0.81	0.22	0.05	1.06	0.17	0.34	354	357	0.36	0.2	5.1
3rd stems	12	50.02	6.35	0.72	42.91	5.91	1.19	20,073	20,029	20.073	335.2	452.6
30/09/2008	24	50.05	5.98	0.44	43.54	4.81	1.32	19,910	19,898	19.925	330.4	458.7
	39	36.69	4.62	0.19	58.50	5.58	1.27	15,193	15,310	15.269	346.8	491.3
Average		45.58	5.65	0.45	48.32	5.43	1.26	18,392	18,412	18.422	337.5	467.5
Std dev		7.70	0.91	0.26	8.83	0.56	0.07	2,772	2,687	2.73	8.4	20.8
4th stems	12	49.64	6.21	0.87	43.28	3.58	1.51	19,874	19,842	19.880	346.2	467.0
08/12/2003	24	50.61	6.20	0.55	42.64	3.21	1.43	20,256	20,229	20.264	345.2	454.1
	39	37.12	4.87	0.33	57.67	2.30	1.29	15,221	15,381	15.319	347.6	459.9
Average		45.79	5.76	0.59	47.86	3.03	1.41	18,451	18,484	18.488	346.3	460.3
Std dev		8.85	0.95	0.38	8.50	0.91	0.16	3,290	3,155	3.23	1.2	6.4
5th stems	12	49.90	5.88	0.25	43.97	6.19	0.88	19,787	19,782	19.805	344.3	459.2
12/10/2009	24	50.29	5.91	0.47	43.33	6.38	1.00	19,990	19,987	20.009	350.2	465.5
	39	47.67	5.52	0.94	45.87	6.47	0.98	18,877	18,876	18.896	345.6	469.2
Average		49.29	5.77	0.56	44.39	6.35	1.26	19,551	19,548	19.570	346.7	464.7
Std dev		1.41	0.21	0.35	1.32	0.14	0.07	593	591	0.59	3.1	5.1
6th stems	12	49.49	5.81	0.34	44.35	6.06	0.99	19,606	19,602	19.625	343.0	459.6
18/01/2010	24	52.93	6.33	0.34	40.40	5.99	0.77	21,331	21,319	21.347	346.1	465.6
	39	50.12	5.98	0.96	42.95	5.80	0.85	20,007	19,998	20.023	346.4	463.4
Average		50.85	6.04	0.55	42.57	5.95	1.41	20,315	20,306	20.332	345.2	462.9
Std dev		0.44	0.12	0.43	2.00	0.18	0.16	283	280	0.28	1.9	3.0

Table B5 Fuel characteristics and Combustion peak temperatures for Treatment N (150Kg N + 80KTable B6 Fuel characteristics and

		dry basos (db)									(°C)	
Sampling	**Plot**	**C**	**H**	**N**	**O**	**Moisture**	**Ash**	**CV (ols) (kJ/kg)**	**CV (pls) (kJ/kg)**	**CV (both) (MJ/kg)**	**T_{vm}**	**T_{char}**
1st leaves	15	46.30	5.46	1.69	46.55	8.31	7.37	18,437	18,438	18.457	309.4	435.8
15/10/2007	20	51.10	6.65	2.17	40.08	7.23	6.96	20,881	20,813	20.870	314.6	428.5
	45	44.19	5.56	2.58	47.67	7.63	6.52	17,765	17,795	17.799	314.4	434.4
Average		47.20	5.89	2.14	44.76	7.72	6.95	19,028	19,015	19.042	312.8	432.9
Std dev		3.54	0.66	0.44	4.10	0.55	0.43	1,640	1,589	1.62	3.0	3.9
3rd leaves	15	50.42	6.45	2.39	40.74	5.77	6.93	20,508	20,462	20.507	325.3	459.1
30/09/2008	20	49.66	6.36	2.49	41.50	5.97	6.87	20,141	20,105	20.145	316.0	449.8
	45	50.69	6.34	2.72	40.24	5.85	6.99	20,631	20,598	20.636	317.6	446.0
Average		50.26	6.38	2.53	40.83	5.86	6.93	20,427	20,388	20.430	319.7	451.6
Std dev		0.54	0.06	0.17	0.63	0.10	0.06	255	255	0.25	5.0	6.7
5th leaves	15	53.63	6.66	2.74	36.96	5.77	8.01	22,168	22,120	22.167	331.2	435.7
12/10/2009	20	50.28	6.35	2.87	40.50	5.97	7.50	20,468	20,433	20.473	321.6	461.4
	45	48.83	6.19	2.07	42.91	5.85	7.32	19,669	19,644	19.678	318.9	485.7
Average		50.91	6.40	2.56	40.12	5.86	7.61	20,768	20,733	20.773	323.9	460.9
Std dev		2.47	0.24	0.43	2.99	0.10	0.36	1,276	1,265	1.27	6.4	25.0
1st stems	15	46.59	5.48	0.52	47.41	5.79	0.95	18,399	18,395	18.416	339.6	454.4
15/10/2007	20	52.19	6.47	0.46	40.89	6.22	1.08	21,080	21,035	21.080	343.8	469.1
	45	53.57	6.09	0.65	39.69	6.22	1.11	21,523	21,568	21.567	337.4	466.7
Average		50.78	6.01	0.54	42.66	6.08	1.05	20,334	20,333	20.354	340.3	463.4
Std dev		3.70	0.50	0.10	4.16	0.25	0.09	1,690	1,699	1.70	3.3	7.9
2nd stems	15	50.99	6.19	2.26	40.56	5.28	0.78	20,639	20,623	20.653	342.5	464.7
11/03/2008	20	48.75	5.22	0.56	45.47	5.32	0.77	19,160	19,184	19.190	340.5	467.0
	45	44.74	5.01	1.68	48.57	5.56	1.05	17,836	17,829	17.850	344.8	470.9
Average		48.16	5.47	1.50	44.86	5.39	0.87	19,212	19,212	19.231	342.6	467.6
Std dev		3.17	0.63	0.86	4.04	0.15	0.16	1,402	1,398	1.40	2.2	3.1
3rd stems	15	49.71	6.06	0.43	43.80	4.97	1.07	19,794	19,773	19.804	339.7	462.2
30/09/2008	20	48.94	5.94	0.37	44.74	5.28	1.02	19,423	19,407	19.436	343.6	464.7
	45	49.57	5.89	0.41	44.14	5.60	1.12	19,674	19,665	19.690	340.1	458.6
Average		49.41	5.96	0.40	44.23	5.28	1.07	19,630	19,615	19.643	341.1	461.8
Std dev		0.41	0.09	0.03	0.48	0.32	0.05	189	188	0.19	2.2	3.1
4th stems	15	49.31	6.15	0.44	44.10	2.20	1.21	19,655	19,626	19.662	345.3	454.6
08/12/2003	20	47.14	5.99	0.39	46.49	1.94	1.29	18,686	18,674	18.701	347.2	457.8
	45	48.47	6.00	0.44	45.08	2.24	1.33	19,253	19,233	19.264	347.6	454.6
Average		48.31	6.05	0.42	45.22	2.13	1.28	19,198	19,177	19.209	346.7	455.7
Std dev		0.60	0.10	0.00	1.20	0.03	0.08	284	278	0.28	1.2	1.8
5th stems	15	49.35	5.77	0.97	43.91	6.26	0.83	19,615	19,615	19.635	331.2	463.2
12/10/2009	20	49.72	5.89	0.97	43.42	6.18	0.78	19,809	19,804	19.827	346.7	469.7
	45	46.27	5.46	0.21	48.06	6.27	0.89	18,236	18,231	18.253	347.9	462.5
Average		48.45	5.70	0.72	45.13	6.24	0.83	19,220	19,217	19.238	341.9	465.1
Std dev		2.18	0.22	0.54	2.55	0.01	0.04	975	978	0.98	9.3	3.9
6th stems	15	50.11	5.87	1.11	42.91	5.95	0.72	19,984	19,985	20.005	343.8	468.7
18/01/2010	20	50.22	6.04	2.03	41.70	6.08	1.01	20,215	20,206	20.232	334.5	436.8
	45	46.58	5.67	0.23	47.52	5.94	1.08	18,387	18,381	18.404	343.5	460.1
Average		48.97	5.86	1.12	44.04	5.99	0.94	19,529	19,524	19.547	340.6	455.2
Std dev		2.50	0.14	0.62	3.07	0.01	0.26	1,130	1,134	1.13	5.3	16.5

Table B6 Fuel characteristics and Combustion peak temperatures for Treatment O (Sewage Pellets)

		dry basos (db)									(°C)	
Sampling	**Plot**	**C**	**H**	**N**	**O**	**Moisture**	**Ash**	**CV (ols) (kJ/kg)**	**CV (pls) (kJ/kg)**	**CV (both) (MJ/kg)**	T_{vm}	T_{char}
1st leaves	8	51.19	5.78	0.46	42.57	7.23	6.16	20,312	20,340	20.346	317.1	462.3
15/10/2007	17	42.64	5.00	0.38	51.98	7.06	6.37	16,066	16,085	16.977	317.1	456.2
	31	46.10	5.36	0.39	48.15	6.98	6.86	17,037	17,036	18.198	316.8	462.0
Average		46.64	5.38	0.41	47.57	7.09	6.46	17,805	17,820	18.507	317.0	460.2
Std dev		4.30	0.39	0.05	4.73	0.13	0.36	2,225	2,233	1.71	0.2	3.4
3rd leaves	8	50.49	6.46	2.87	40.18	6.26	8.00	20,608	20,563	20.608	323.4	459.6
30/09/2008	17	50.98	7.06	2.92	39.04	6.02	7.14	19,465	19,434	21.066	311.8	423.0
	31	37.88	4.98	1.88	55.26	6.02	7.55	15,051	15,246	15.706	327.2	491.2
Average		46.45	6.17	2.56	44.82	6.10	7.56	18,375	18,414	19.126	320.8	457.9
Std dev		7.43	1.07	0.59	9.05	0.14	0.43	2,934	2,801	2.97	8.0	34.1
5th leaves	8	46.22	5.92	2.31	45.54	6.26	7.52	18,549	18,556	18.573	306.3	438.0
12/10/2009	17	47.41	6.00	2.13	44.46	6.02	7.98	17,831	17,856	19.045	316.2	445.0
	31	49.12	6.33	1.97	42.58	6.02	6.96	18,467	18,473	19.830	328.3	436.6
Average		47.58	6.08	2.14	44.19	6.10	7.49	18,282	18,295	19.150	316.9	439.9
Std dev		1.45	0.22	0.17	1.50	0.14	0.51	393	383	0.63	11.0	4.5
1st stems	8	41.99	4.48	0.30	53.23	6.06	0.90	16,806	16,761	16.799	341.2	468.7
15/10/2007	17	52.41	5.68	0.57	41.33	5.48	0.58	20,788	20,861	20.844	339.2	454.4
	31	58.43	6.55	0.61	34.40	5.38	0.99	24,149	24,282	24.239	341.7	462.0
Average		50.95	5.57	0.49	42.99	5.64	0.82	20,581	20,635	20.627	340.7	461.7
Std dev		8.32	1.04	0.17	9.52	0.37	0.22	3,676	3,766	3.72	1.3	7.1
2nd stems	8	51.57	5.87	2.69	39.86	5.32	0.89	20,804	20,837	20.841	343.6	475.7
11/03/2008	17	45.41	5.16	1.76	47.67	5.11	0.62	18,090	18,087	18.106	341.4	461.1
	31	48.89	5.95	0.57	44.59	5.05	1.18	19,430	19,413	19.442	343.4	472.7
Average		48.62	5.66	1.67	44.04	5.16	0.90	19,441	19,446	19.463	342.8	469.8
Std dev		3.09	0.43	1.06	3.93	0.14	0.28	1,357	1,376	1.37	1.2	7.7
3rd stems	8	49.95	6.16	0.54	43.36	5.98	1.24	19,947	19,920	19.955	344.0	464.1
30/09/2008	17	49.37	5.98	0.55	44.10	5.83	1.12	19,641	19,624	19.653	330.0	428.9
	31	36.99	4.58	0.23	58.19	5.71	0.97	15,301	15,397	15.366	354.6	466.9
Average		45.44	5.57	0.44	48.55	5.84	1.11	18,296	18,314	18.325	342.9	453.3
Std dev		7.32	0.86	0.18	8.36	0.14	0.14	2,599	2,530	2.57	12.3	21.2
4th stems	8	49.91	6.20	0.50	43.40	2.39	1.21	19,939	19,908	19.945	345.8	467.0
08/12/2003	17	49.13	6.12	1.02	43.72	2.70	1.33	19,646	19,621	19.655	336.5	432.6
	31	36.58	4.62	0.35	58.46	2.08	1.23	15,182	15,305	15.261	337.6	433.9
Average		45.21	5.65	0.62	48.52	2.39	1.26	18,256	18,278	18.287	340.0	444.5
Std dev		9.42	1.12	0.11	8.60	0.22	0.01	3,364	3,254	3.31	5.1	19.5
5th stems	8	43.91	5.44	0.18	50.47	2.39	0.84	17,352	17,370	17.380	340.1	437.3
12/10/2009	17	47.48	5.85	0.39	46.28	2.70	0.97	18,800	18,788	18.815	345.1	458.4
	31	46.02	5.82	0.20	47.96	2.08	0.55	18,182	18,182	18.202	349.5	467.1
Average		45.80	5.70	0.26	48.24	2.39	0.79	18,111	18,113	18.132	344.9	454.3
Std dev		1.49	0.27	0.01	2.11	0.22	0.20	586	574	0.58	4.7	15.4
6th stems	8	44.08	5.50	0.24	50.18	2.39	0.99	17,422	17,442	17.451	342.9	465.1
18/01/2010	17	46.96	5.74	0.29	47.01	2.70	0.78	18,556	18,548	18.572	343.6	451.3
	31	46.40	5.82	0.13	47.65	2.08	0.52	18,323	18,319	18.342	345.2	450.9
Average		45.81	5.69	0.22	48.28	2.39	0.77	18,101	18,103	18.122	343.9	455.8
Std dev		1.63	0.22	0.07	1.67	0.22	0.33	637	620	0.63	1.2	8.1

APPENDIX C: Metal Analysis for SRC Willow

Table C1 Metal content in SRC Willow raw fuel for Treatment A (0 Kg N)

Sampling	Plot	Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Ti	Zn
1st leaves	7	60.5	10096	1.00	0.16	0.27	5.13	90.6	20140	2761	47.7	0.75	389.5	1.26	5014	0.38	2374	2.10	154.3
15/10/2007	21	110.8	13304	1.55	0.19	0.48	5.03	132.8	16115	3666	48.2	0.44	404.6	1.25	5034	0.78	2318	3.17	171.8
	44	69.8	8361	1.53	0.24	0.38	5.28	117.1	20948	1929	142.8	0.52	612.3	1.21	4306	0.78	2111	2.42	231.7
Average		80.4	10587	1.36	0.20	0.38	5.14	113.5	19068	2785	79.5	0.57	468.8	1.24	4785	0.65	2268	2.56	185.9
Std dev		26.8	2508	0.31	0.04	0.10	0.13	21.3	2589	869	54.8	0.16	124.5	0.03	415	0.23	139	0.55	40.6
3rd leaves	7	43.4	14332	2.32	0.16	0.00	9.07	80.9	16712	3810	89.8	0.48	325.7	4.54	10154	0.83	2602	1.07	499.0
30/09/2008	21	40.4	18458	4.79	0.22	0.00	10.21	82.0	13843	4624	98.9	0.47	231.1	5.05	9845	0.96	2473	1.21	614.9
	44	63.6	9909	2.15	0.41	0.00	7.35	105.4	18597	2636	469.2	0.46	324.9	2.75	7334	2.03	2491	1.33	458.2
Average		49.1	14233	3.09	0.26	0.00	8.88	89.4	16384	3690	219.3	0.47	293.9	4.11	9111	1.27	2522	1.20	524.0
Std dev		12.6	4275	1.48	0.13	0.00	1.44	13.8	2394	999	216.5	0.01	54.4	1.21	1547	0.66	70	0.13	81.3
5th leaves	7	49.5	17558	2.14	0.27	0.93	6.16	65.4	12698	5086	56.3	1.19	671.1	2.70	9832	0.44	3639	0.96	277.7
12/10/2009	21	44.9	20789	5.08	0.28	0.89	5.93	57.6	12510	5304	71.7	0.89	458.9	2.97	10292	0.33	2155	0.59	473.5
	44	60.9	15094	2.24	0.44	0.78	5.52	83.3	14306	3856	569.4	0.74	731.0	2.23	6636	0.55	3865	0.86	283.5
Average		51.8	17814	3.15	0.33	0.87	5.87	68.8	13171	4749	232.4	0.94	620.3	2.63	8920	0.44	3220	0.80	344.9
Std dev		8.2	2856	1.67	0.10	0.08	0.33	13.2	987	780	291.9	0.23	143.0	0.38	1992	0.11	929	0.19	111.4
1st stems	7	11.5	2356	0.67	0.02	0.08	3.40	30.3	3343	659	10.7	0.04	9.2	0.18	952	0.00	361	0.07	70.11
15/10/2007	21	15.0	2207	0.79	0.02	0.00	3.29	52.0	3194	625	7.3	0.03	1.5	0.15	891	0.10	310	0.08	64.68
	44	10.6	2194	0.91	0.01	0.14	3.38	33.4	3077	621	33.1	0.00	8.1	0.09	1012	0.37	418	0.05	92.54
Average		12.4	2252	0.79	0.02	0.07	3.36	38.6	3205	635	17.0	0.02	6.3	0.14	952	0.16	363	0.06	75.8
Std dev		2.3	90	0.12	0.01	0.07	0.06	11.7	133	21	14.0	0.02	4.1	0.05	60	0.19	54	0.02	14.8
2nd stems	7	7.5	2285	0.64	0.00	0.02	3.03	13.1	2947	676	13.3	0.02	22.5	0.19	927	0.12	367	0.00	71.25
11/03/2008	21	20.7	2211	0.80	0.00	0.07	3.14	12.2	2787	650	8.7	0.02	16.9	0.16	954	0.07	327	0.34	74.48
	44	12.4	2586	1.61	0.00	0.04	4.94	18.7	3144	734	92.0	0.00	40.1	0.16	1245	0.11	462	0.32	153.75
Average		13.6	2361	1.02	0.00	0.04	3.71	14.6	2960	687	38.0	0.01	26.5	0.17	1042	0.10	386	0.22	99.8
Std dev		6.7	199	0.52	0.00	0.03	1.07	3.5	179	43	46.8	0.01	12.1	0.02	176	0.03	69	0.19	46.7
3rd stems	7	9.2	2574	1.32	0.00	0.15	4.11	16.2	2752	734	11.2	0.01	0.0	0.23	1165	0.00	358	0.03	124.92
30/09/2008	21	7.8	2774	1.79	0.00	0.00	3.62	23.8	2290	721	10.6	0.07	5.8	0.18	973	0.00	335	0.09	121.04
	44	9.0	2444	1.74	0.16	0.00	3.17	16.0	2832	638	73.0	0.01	21.5	0.21	1029	0.42	330	0.11	149.45
Average		8.7	2597	1.62	0.05	0.05	3.63	18.7	2625	698	31.6	0.03	9.1	0.21	1056	0.14	341	0.08	131.8
Std dev		0.8	167	0.26	0.09	0.09	0.47	4.4	293	52	35.9	0.03	11.1	0.02	99	0.24	15	0.04	15.4
4th stems	7	4.7	2276	0.97	0.00	0.00	3.46	10.2	2273	650	8.6	0.00	16.8	0.07	974	0.00	324	0.00	104.52
08/12/2003	21	8.7	3158	1.76	0.00	0.00	4.66	12.3	2514	818	12.6	0.00	24.7	0.15	1012	0.00	386	0.00	130.29
	44	11.1	2189	1.77	0.03	0.00	3.23	14.5	2668	621	85.2	0.05	24.0	0.09	976	0.00	350	0.63	148.06
Average		8.2	2541	1.50	0.01	0.00	3.78	12.4	2485	696	35.5	0.02	21.9	0.10	987	0.00	353	0.21	127.6
Std dev		3.2	536	0.46	0.02	0.00	0.77	2.2	199	106	43.1	0.03	4.3	0.04	21	0.00	31	0.36	21.9
5th stems	7	5.0	2452	1.00	0.00	0.42	3.35	7.9	2256	699	5.90	0.00	5.0	0.09	941	0.17	276	0.00	102.05
12/10/2009	21	7.0	3518	2.06	0.00	0.52	4.06	9.9	2322	819	7.46	0.00	6.1	0.10	1033	0.31	312	0.00	133.13
	44	14.1	2827	1.33	0.04	0.52	3.29	16.2	2962	735	57.94	0.00	16.4	0.26	1134	0.31	375	0.02	114.92
Average		8.7	2933	1.46	0.01	0.49	3.57	11.3	2513	751	23.8	0.00	9.2	0.15	1036	0.26	321	0.01	116.7
Std dev		4.8	540	0.54	0.02	0.06	0.43	4.4	390	62	29.6	0.00	6.3	0.10	97	0.08	50	0.01	15.6
6th stems	7	7.2	2591	1.04	0.00	0.00	3.15	6.0	2426	663	6.03	0.00	15.3	0.07	958	0.00	312	0.00	98.46
18/01/2010	21	10.7	2626	0.89	0.00	0.00	3.40	12.3	2346	673	6.48	0.00	22.3	0.00	984	0.00	313	0.00	91.07
	44	14.9	2285	1.24	0.00	0.00	3.64	9.7	2122	617	5.79	0.00	21.5	0.12	903	0.00	254	0.00	80.80
Average		10.9	2501	1.06	0.00	0.00	3.40	9.4	2298	651	6.1	0.00	19.7	0.06	948	0.00	293	0.00	90.1
Std dev		3.9	188	0.18	0.00	0.00	0.24	3.2	158	30	0.4	0.00	3.8	0.06	42	0.00	34	0.00	8.9

Table C2 Metal content in SRC Willow raw fuel for Treatment D (150 Kg N)

Sampling	Plot	Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Ti	Zn
1st leaves	14	90.2	10231	0.70	0.17	0.34	5.75	130.0	21632	2636	60.4	0.95	403.2	1.88	3298	0.81	1752	3.18	37.7
15/10/2007	16	76.8	12743	0.76	0.12	0.28	6.00	96.4	18302	3257	27.9	0.54	356.5	1.27	4442	0.48	2478	2.06	45.3
	32	47.2	11122	0.60	0.18	0.16	3.89	78.8	22090	3112	30.2	0.69	558.9	0.94	2316	0.33	1820	1.60	29.7
Average		71.4	11365	0.69	0.16	0.26	5.22	101.8	20675	3002	39.5	0.73	439.5	1.37	3352	0.54	2017	2.28	37.6
Std dev		22.0	1274	0.08	0.03	0.09	1.15	26.0	2067	324	18.1	0.21	106.0	0.47	1064	0.24	401	0.81	7.8
3rd leaves	14	77.0	12781	1.16	0.28	0.00	6.91	107.0	16368	3391	112.9	0.66	388.2	2.76	5754	1.10	2392	1.85	153.7
30/09/2008	16	81.3	14619	0.90	0.26	0.00	8.58	121.3	18269	3982	34.1	1.57	268.3	4.36	5013	1.01	3686	2.27	124.0
	32	56.8	12372	1.09	0.17	0.00	8.80	102.2	18604	3390	55.0	0.52	347.7	2.63	5229	1.31	2831	1.65	212.9
Average		71.7	13257	1.05	0.23	0.00	8.10	110.2	17747	3588	67.3	0.92	334.7	3.25	5332	1.14	2970	1.92	163.5
Std dev		13.1	1197	0.13	0.06	0.00	1.03	9.9	1206	342	40.8	0.57	61.0	0.96	381	0.15	658	0.32	45.2
5th leaves	14	54.1	13616	0.87	0.26	0.82	3.97	72.2	16690	3053	80.8	1.09	876.4	1.28	5730	0.47	1994	1.03	107.5
12/10/2009	16	55.0	21669	1.98	0.24	0.88	6.08	76.7	11150	4998	52.1	1.49	580.4	2.45	8187	0.21	3190	0.93	268.2
	32	51.6	13974	1.32	0.22	0.89	4.85	69.0	18152	3582	55.3	0.52	658.5	1.53	4854	0.40	2109	0.77	158.5
Average		53.6	16419	1.39	0.24	0.86	4.97	72.6	15331	3878	62.7	1.03	705.1	1.75	6257	0.36	2431	0.91	178.1
Std dev		1.8	4550	0.56	0.02	0.04	1.06	3.9	3694	1005	15.7	0.49	153.4	0.62	1728	0.13	660	0.13	82.1
1st stems	14	9.8	2169	0.46	0.03	0.06	3.11	79.1	3883	677	11.9	0.07	14.7	0.32	1125	0.12	396	0.67	37.70
15/10/2007	16	11.1	2129	0.36	0.02	0.02	2.81	23.7	3328	594	3.9	0.07	15.8	0.18	962	0.14	398	0.07	32.11
	32	26.1	2210	0.40	0.01	0.00	2.54	47.4	3272	665	5.6	0.01	8.3	0.20	1011	0.03	418	0.08	37.78
Average		15.7	2169	0.41	0.02	0.03	2.82	50.1	3494	645	7.1	0.05	13.0	0.24	1033	0.10	404	0.27	35.9
Std dev		9.1	41	0.05	0.01	0.03	0.28	27.8	338	45	4.3	0.03	4.0	0.08	84	0.06	12	0.34	3.2
2nd stems	14	384.2	3532	0.49	0.30	1.24	4.37	1070.3	3009	597	29.2	0.08	53.5	1.10	947	3.71	553	8.30	46.17
11/03/2008	16	12.1	2272	0.40	0.00	0.03	3.02	15.7	2770	618	5.0	0.00	30.2	0.15	924	0.03	433	0.30	39.64
	32	24.0	2616	0.49	0.00	0.12	2.51	62.7	2633	701	6.4	0.04	35.6	0.14	828	0.40	406	1.32	42.28
Average		140.1	2807	0.46	0.10	0.46	3.30	382.9	2804	639	13.5	0.04	39.8	0.46	900	1.38	464	3.31	42.7
Std dev		211.5	651	0.05	0.17	0.67	0.96	595.8	190	55	13.5	0.04	12.2	0.55	63	2.03	79	4.36	3.3
3rd stems	14	6.2	2345	0.61	0.12	0.61	3.88	12.6	2329	611	14.6	0.25	3.0	0.28	857	0.20	276	0.18	58.79
30/09/2008	16	7.5	2464	0.22	0.02	0.00	2.56	31.5	2756	567	4.9	0.08	6.6	0.23	870	0.00	343	0.18	46.72
	32	9.3	2525	0.40	0.00	0.00	2.73	12.8	2522	631	7.5	0.01	9.4	0.13	866	0.00	317	0.08	68.11
Average		7.7	2445	0.41	0.05	0.20	3.05	19.0	2536	603	9.0	0.11	6.3	0.21	864	0.07	312	0.15	57.9
Std dev		1.5	92	0.19	0.07	0.35	0.72	10.9	214	33	5.0	0.12	3.2	0.08	7	0.11	34	0.06	10.7
4th stems	14	4.0	2322	0.49	0.00	0.00	2.23	10.4	2460	576	12.0	0.00	22.5	0.00	812	0.00	280	0.00	48.88
08/12/2003	16	6.7	2532	0.42	0.00	0.00	2.81	9.3	2554	584	5.5	0.00	20.6	0.11	830	0.00	355	0.00	56.74
	32	3.7	2508	0.65	0.00	0.00	2.93	10.4	2566	634	8.1	0.00	21.1	0.00	853	0.00	345	0.00	65.83
Average		4.8	2454	0.52	0.00	0.00	2.66	10.1	2527	598	8.5	0.00	21.4	0.04	832	0.00	327	0.00	57.1
Std dev		1.7	115	0.12	0.00	0.00	0.38	0.6	58	32	3.2	0.00	1.0	0.06	20	0.00	41	0.00	8.5
5th stems	14	4.9	2517	0.54	0.00	0.66	2.54	9.9	1982	603	10.41	0.00	6.6	0.00	801	0.27	234	0.00	52.67
12/10/2009	16	8.5	3398	0.72	0.00	0.52	3.70	10.4	2771	743	6.03	0.00	14.8	0.13	985	0.29	346	0.00	80.86
	32	15.6	2753	0.82	0.10	0.46	2.49	14.6	2380	671	6.72	0.31	14.9	0.16	885	0.19	286	0.19	56.82
Average		9.6	2890	0.69	0.03	0.55	2.91	11.6	2378	672	7.7	0.10	12.1	0.10	891	0.25	288	0.06	63.5
Std dev		5.4	456	0.14	0.06	0.11	0.69	2.6	395	70	2.4	0.18	4.7	0.09	92	0.05	56	0.11	15.2
6th stems	14	5.3	2064	0.51	0.00	0.00	2.36	4.5	1975	525	11.76	0.00	13.4	0.00	766	0.00	233	0.00	54.31
18/01/2010	16	4.6	2237	0.46	0.00	0.00	2.63	6.1	2197	558	4.62	0.00	14.5	0.04	792	0.00	261	0.00	55.15
	32	5.9	2862	0.89	0.00	0.00	2.89	7.6	2459	699	7.02	0.00	21.7	0.51	946	0.00	305	0.00	82.58
Average		5.3	2388	0.62	0.00	0.00	2.63	6.1	2210	594	7.8	0.00	16.5	0.18	835	0.00	266	0.00	64.0
Std dev		0.7	420	0.23	0.00	0.00	0.26	1.5	242	92	3.6	0.00	4.6	0.28	97	0.00	36	0.00	16.1

Table C3 Metal content in SRC Willow raw fuel for Treatment F (250 Kg N)

Sampling	Plot	Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Ti	Zn
1st leaves	6	43.2	8668	0.65	0.12	0.14	5.43	67.0	15566	2203	29.8	0.44	279.2	1.07	3119	0.29	1430	1.16	60.8
15/10/2007	26	61.7	13658	1.02	0.15	0.29	6.72	99.9	15423	3749	41.0	0.60	427.6	1.81	3824	0.55	2315	2.27	56.8
	36	42.8	9587	0.48	0.19	0.13	3.66	66.9	21353	2776	32.4	0.58	436.6	0.90	2489	0.37	1734	1.13	25.7
Average		49.2	10638	0.72	0.15	0.18	5.27	77.9	17447	2909	34.4	0.54	381.1	1.26	3144	0.40	1827	1.52	47.7
Std dev		10.8	2656	0.28	0.04	0.09	1.54	19.0	3384	782	5.9	0.08	88.4	0.48	668	0.13	450	0.65	19.2
3rd leaves	6	44.2	16631	1.16	0.18	0.00	12.28	96.0	22017	3305	61.3	1.47	190.6	5.49	5850	0.78	5090	1.38	226.5
30/09/2008	26	47.0	16651	1.27	0.25	0.00	8.73	96.1	16310	4692	48.1	0.73	276.1	3.62	6278	1.24	3355	1.24	196.9
	36	51.7	12375	0.82	0.35	0.20	6.33	103.0	17270	2990	33.7	1.09	406.2	1.77	3981	1.84	3344	1.60	81.2
Average		47.6	15219	1.08	0.26	0.07	9.11	98.4	18532	3662	47.7	1.09	291.0	3.63	5370	1.29	3929	1.41	168.2
Std dev		3.8	2463	0.23	0.08	0.12	3.00	4.0	3056	906	13.8	0.37	108.5	1.86	1222	0.53	1005	0.18	76.8
5th leaves	6	39.8	20536	1.28	0.17	0.59	5.33	57.6	13106	4901	77.9	0.98	602.9	1.76	7239	0.07	3942	0.46	201.0
12/10/2009	26	53.7	14020	1.19	0.22	0.75	4.47	75.5	13799	3716	48.7	0.46	601.7	1.07	4813	0.30	1801	0.98	167.4
	36	51.6	12547	0.73	0.38	0.78	4.50	74.8	16452	3507	89.4	0.67	702.2	0.81	4258	0.51	2944	0.86	100.0
Average		48.4	15701	1.07	0.25	0.71	4.77	69.3	14452	4041	72.0	0.70	635.6	1.21	5437	0.29	2895	0.76	156.2
Std dev		7.5	4251	0.30	0.11	0.11	0.49	10.1	1766	752	21.0	0.26	57.7	0.49	1585	0.22	1071	0.27	51.4
1st stems	6	6.0	1977	0.31	0.02	0.02	3.05	27.6	3579	572	6.4	0.03	13.3	0.20	1085	0.08	417	0.06	42.24
15/10/2007	26	14.7	2257	0.47	0.00	0.06	3.46	60.4	3263	613	5.4	0.01	12.1	0.21	979	0.26	386	0.09	36.72
	36	23.0	2019	0.31	0.03	0.00	6.03	27.8	3514	638	5.9	0.00	10.0	0.18	1006	0.21	433	0.02	33.24
Average		14.6	2084	0.36	0.02	0.03	4.18	38.6	3452	608	5.9	0.02	11.8	0.20	1023	0.18	412	0.06	37.4
Std dev		8.5	151	0.09	0.01	0.03	1.62	18.9	167	34	0.5	0.02	1.7	0.01	55	0.09	24	0.03	4.5
2nd stems	6	13.4	2692	0.41	0.00	0.04	3.00	19.4	3434	725	8.4	0.04	40.3	0.26	1165	0.12	528	0.00	48.54
11/03/2008	26	12.1	2694	0.44	0.00	0.05	3.49	15.9	2894	753	5.3	0.03	58.0	0.21	1007	0.00	463	0.47	38.43
	36	14.0	2367	0.25	0.00	0.02	2.19	16.9	2491	655	3.8	0.01	29.4	0.13	882	0.01	424	0.34	26.89
Average		13.2	2585	0.37	0.00	0.03	2.90	17.4	2940	711	5.9	0.03	42.6	0.20	1018	0.04	472	0.27	38.0
Std dev		1.0	188	0.10	0.00	0.02	0.66	1.8	473	50	2.3	0.02	14.4	0.06	142	0.07	53	0.24	10.8
3rd stems	6	14.1	3583	0.79	0.00	0.35	4.99	47.9	3442	813	10.8	0.07	1.1	0.30	1368	0.00	525	0.31	88.38
30/09/2008	26	11.5	2857	0.40	0.01	0.00	3.20	36.0	2828	706	7.0	0.01	16.6	0.21	922	0.00	362	0.15	59.90
	36	11.1	2317	0.52	0.00	0.00	2.65	16.5	2192	616	7.8	0.06	11.0	0.14	865	0.00	305	0.07	69.38
Average		12.3	2919	0.57	0.00	0.12	3.61	33.5	2821	712	8.5	0.04	9.6	0.22	1052	0.00	397	0.18	72.6
Std dev		1.6	636	0.20	0.01	0.20	1.22	15.9	625	99	2.0	0.03	7.9	0.08	275	0.00	114	0.13	14.5
4th stems	6	8.0	2348	0.29	0.00	0.00	3.06	10.9	2497	563	10.0	0.00	17.3	0.10	899	0.00	380	0.00	58.73
08/12/2003	26	7.6	2693	0.41	0.00	0.00	2.83	8.3	2685	659	5.4	0.00	23.8	0.04	872	0.00	354	0.00	48.78
	36	8.7	2599	0.30	0.00	0.00	2.35	10.9	2817	660	6.3	0.00	25.8	0.00	843	0.00	364	0.00	55.91
Average		8.1	2547	0.34	0.00	0.00	2.75	10.0	2666	628	7.2	0.00	22.3	0.05	871	0.00	366	0.00	54.5
Std dev		0.6	178	0.07	0.00	0.00	0.36	1.5	161	56	2.4	0.00	4.5	0.05	28	0.00	13	0.00	5.1
5th stems	6	4.5	2580	0.44	0.00	0.41	2.47	8.5	2242	579	7.23	0.00	5.0	0.05	779	0.23	273	0.00	60.91
12/10/2009	26	11.0	2929	0.64	0.02	0.51	1.99	13.2	2255	698	5.65	0.00	13.0	0.06	825	0.10	273	0.08	50.06
	36	10.2	2756	0.60	0.02	0.60	2.04	11.3	2342	659	9.13	0.00	12.7	0.09	856	0.32	289	0.04	48.33
Average		8.6	2755	0.56	0.02	0.50	2.17	11.0	2279	645	7.3	0.00	10.2	0.07	820	0.21	278	0.04	53.1
Std dev		3.5	175	0.10	0.01	0.10	0.27	2.3	54	61	1.7	0.00	4.5	0.02	39	0.11	9	0.04	6.8
6th stems	6	13.1	2621	0.48	0.00	0.00	2.58	14.0	2385	609	7.04	0.00	26.0	0.06	822	0.00	306	0.02	65.39
18/01/2010	26	10.1	3886	0.55	0.00	0.00	2.51	13.0	2765	735	7.15	0.00	33.4	0.00	945	0.00	318	0.00	63.12
	36	7.5	2883	0.20	0.00	0.00	1.64	14.2	2613	610	5.73	0.00	25.3	0.00	890	0.00	306	0.00	41.94
Average		10.2	3130	0.41	0.00	0.00	2.24	13.8	2587	652	6.6	0.00	28.2	0.02	886	0.00	310	0.01	56.8
Std dev		2.8	668	0.18	0.00	0.00	0.52	0.7	191	72	0.8	0.00	4.5	0.04	61	0.00	7	0.01	12.9

Table C4 Metal content in SRC Willow raw fuel for Treatment J (150Kg N + 100Kg K)

Sampling	Plot	Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Ti	Zn
1st leaves	12	59.6	9964	0.52	0.12	0.26	6.88	90.1	21837	2421	29.9	1.22	371.1	1.72	3130	0.41	2474	1.92	48.9
15/10/2007	24	59.3	9436	1.31	0.14	0.26	6.03	87.6	21434	2105	85.3	0.66	355.5	1.98	3316	0.61	1887	2.11	104.8
	39	59.8	10052	0.94	0.17	0.31	4.64	98.6	18160	3143	73.8	0.68	512.7	1.03	2971	0.48	1451	2.00	92.5
Average		59.6	9817	0.92	0.14	0.27	5.85	92.1	20477	2557	63.0	0.85	413.1	1.57	3139	0.50	1937	2.01	82.1
Std dev		0.2	333	0.39	0.02	0.03	1.13	5.8	2017	532	29.2	0.32	86.6	0.49	173	0.10	513	0.10	29.4
3rd leaves	12	36.2	11101	0.64	0.18	-0.09	8.51	86.4	19974	3194	33.9	1.76	267.7	3.29	4487	0.92	3807	1.08	104.4
30/09/2008	24	75.4	12069	1.35	0.12	0.05	8.22	125.5	19478	2874	210.8	0.65	434.4	4.25	5885	0.57	2614	1.90	253.3
	39	41.9	11263	1.14	0.23	-0.30	7.07	82.9	17381	2676	174.3	0.64	370.6	2.53	5286	1.66	2293	1.08	235.8
Average		51.2	11478	1.04	0.18	-0.11	7.93	98.3	18945	2915	139.7	1.02	357.5	3.36	5219	1.05	2905	1.36	197.8
Std dev		21.2	519	0.36	0.05	0.17	0.76	23.6	1377	261	93.4	0.64	84.1	0.86	701	0.56	798	0.47	81.4
5th leaves	12	37.6	13263	1.31	0.18	1.24	4.86	59.3	21948	3260	41.8	1.09	558.5	1.31	5646	2.47	2734	0.53	149.9
12/10/2009	24	41.4	16005	1.80	0.35	0.72	5.59	62.8	14383	3605	150.8	1.20	463.5	4.02	6656	0.14	2897	0.82	215.8
	39	42.8	18099	2.25	0.20	0.84	5.98	65.7	16461	4350	141.1	0.96	549.9	2.87	9219	0.37	2721	0.38	281.5
Average		40.6	15789	1.78	0.24	0.93	5.47	62.6	17597	3738	111.2	1.08	524.0	2.73	7173	0.99	2784	0.58	215.7
Std dev		2.7	2425	0.47	0.09	0.27	0.56	3.2	3908	557	60.3	0.12	52.6	1.36	1842	1.28	98	0.22	65.8
1st stems	12	7.3	2084	0.38	0.02	0.22	3.52	34.7	3556	638	5.0	0.12	16.4	0.25	1000	0.04	429	0.07	46.73
15/10/2007	24	11.8	2054	0.59	0.01	0.09	3.31	27.9	3710	582	17.9	0.00	13.6	0.28	997	0.17	388	0.18	59.42
	39	25.3	1986	0.58	0.01	0.02	4.34	26.5	3117	588	14.3	0.00	5.5	0.16	930	0.26	307	0.00	49.09
Average		14.8	2041	0.52	0.01	0.11	3.73	29.7	3461	603	12.4	0.04	11.8	0.23	975	0.16	375	0.08	51.7
Std dev		9.3	51	0.12	0.01	0.10	0.55	4.4	308	31	6.7	0.07	5.7	0.07	40	0.11	62	0.09	6.7
2nd stems	12	21.5	2412	0.39	0.00	0.58	4.13	23.6	2659	680	6.0	0.10	29.5	0.20	949	2.59	466	0.47	56.68
11/03/2008	24	18.1	2783	0.69	0.02	0.07	3.90	26.4	3287	722	27.6	0.01	38.8	0.31	1057	0.14	489	0.33	68.28
	39	19.2	2018	0.54	0.00	0.06	2.78	17.5	3095	633	16.8	0.00	37.8	0.18	944	0.23	370	0.37	54.46
Average		19.6	2405	0.54	0.01	0.24	3.60	22.5	3014	678	16.8	0.03	35.4	0.23	983	0.99	442	0.39	59.8
Std dev		1.7	383	0.15	0.01	0.30	0.72	4.6	322	45	10.8	0.05	5.1	0.07	64	1.39	63	0.07	7.4
3rd stems	12	8.9	2612	0.50	0.00	0.03	3.48	17.1	3359	679	6.2	0.05	2.5	0.21	1029	0.00	430	0.03	72.76
30/09/2008	24	11.3	2649	0.56	0.02	0.00	2.80	20.9	2974	592	30.2	0.04	10.9	0.25	963	0.00	335	0.00	80.54
	39	5.8	2304	0.48	0.01	0.00	2.80	14.3	2691	578	26.8	0.02	10.3	0.19	871	0.00	314	0.00	77.60
Average		8.7	2522	0.51	0.01	0.01	3.03	17.4	3008	616	21.1	0.03	7.9	0.22	954	0.00	360	0.01	77.0
Std dev		2.8	189	0.04	0.01	0.02	0.39	3.3	335	55	13.0	0.02	4.7	0.03	79	0.00	62	0.02	3.9
4th stems	12	9.8	2230	0.25	0.00	0.00	2.64	10.1	2911	572	7.1	0.00	17.9	0.05	825	0.00	399	0.00	62.00
08/12/2003	24	6.3	2760	0.79	0.00	0.00	3.45	12.0	2945	618	23.1	0.00	37.5	0.21	921	0.00	359	0.00	84.63
	39	7.4	2349	0.76	0.00	0.00	2.70	7.8	2381	601	13.0	0.00	17.8	0.00	865	0.00	309	0.00	76.96
Average		7.8	2446	0.60	0.00	0.00	2.93	10.0	2746	597	14.4	0.00	24.4	0.09	871	0.00	356	0.00	74.5
Std dev		1.8	278	0.30	0.00	0.00	0.45	2.1	316	23	8.1	0.00	11.4	0.11	48	0.00	45	0.00	11.5
5th stems	12	11.3	2213	0.38	0.00	0.58	2.49	27.1	2233	534	4.96	0.00	5.8	0.00	774	0.29	272	0.00	58.34
12/10/2009	24	5.1	2904	0.97	0.00	0.44	3.71	9.0	2572	646	19.05	0.00	6.7	0.17	884	0.54	294	0.00	84.11
	39	10.1	3453	1.42	0.01	0.42	4.07	14.5	3236	849	16.44	0.00	16.0	0.28	1179	0.20	393	0.02	109.91
Average		8.8	2857	0.92	0.00	0.48	3.43	16.9	2680	676	13.5	0.00	9.5	0.15	946	0.35	320	0.01	84.1
Std dev		3.3	621	0.52	0.00	0.09	0.83	9.3	510	160	7.5	0.00	5.6	0.14	209	0.18	65	0.01	25.8
6th stems	12	10.4	1910	0.29	0.00	0.00	2.92	7.9	2500	492	3.99	0.00	22.8	0.01	749	0.00	321	0.00	55.57
18/01/2010	24	5.2	2680	0.66	0.00	0.00	2.80	6.8	2441	605	21.90	0.00	18.6	0.05	918	0.00	318	0.00	76.16
	39	7.1	2598	0.65	0.00	0.00	2.49	7.2	2378	593	13.00	0.00	17.1	0.02	896	0.00	279	0.00	73.07
Average		7.5	2396	0.53	0.00	0.00	2.74	7.3	2439	563	13.0	0.00	19.5	0.03	854	0.00	306	0.00	68.3
Std dev		2.6	423	0.21	0.00	0.00	0.23	0.6	61	62	9.0	0.00	3.0	0.02	92	0.00	23	0.00	11.1

Table C5 Metal content in SRC Willow raw fuel for Treatment N (150Kg N + 80Kg S)

Sampling	Plot	Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Ti	Zn
1st leaves	15	51.0	9125	0.45	0.29	0.26	4.82	82.0	27558	2132	28.6	0.99	511.5	1.31	2067	0.40	2628	1.93	19.7
15/10/2007	20	60.7	11543	0.62	0.24	0.21	4.79	90.2	22620	2917	26.8	0.50	529.5	1.56	3111	0.50	3018	2.07	27.2
	45	54.3	9677	1.31	0.15	0.22	6.88	98.7	20278	2049	133.4	0.62	407.2	2.24	2931	0.46	3224	1.59	144.5
Average		55.3	10115	0.79	0.23	0.23	5.50	90.3	23485	2366	62.9	0.70	482.7	1.70	2703	0.45	2957	1.86	63.8
Std dev		5.0	1267	0.45	0.07	0.03	1.20	8.3	3716	479	61.0	0.26	66.0	0.48	558	0.05	303	0.25	70.0
3rd leaves	15	42.2	13636	1.09	0.25	0.18	6.89	78.6	15602	3822	61.5	0.44	349.8	2.55	5535	1.08	2853	1.26	106.1
30/09/2008	20	45.9	12724	1.26	0.27	0.29	6.89	85.2	16789	3384	142.9	0.39	421.9	2.64	6312	1.09	2601	1.17	151.4
	45	49.9	9454	1.33	0.34	0.37	7.37	82.9	18254	2576	294.1	0.62	360.5	3.03	5196	1.55	2616	1.14	353.4
Average		46.0	11938	1.23	0.28	0.28	7.05	82.2	16882	3261	166.2	0.48	377.4	2.74	5681	1.24	2690	1.19	203.6
Std dev		3.9	2199	0.12	0.05	0.09	0.28	3.4	1328	632	118.0	0.12	38.9	0.26	572	0.27	142	0.06	131.7
5th leaves	15	162.9	14856	0.71	0.33	0.95	3.62	165.4	16983	4823	92.2	0.35	805.6	0.77	4174	0.96	1953	3.16	30.2
12/10/2009	20	64.7	17717	1.37	0.30	0.98	5.11	84.3	18092	4192	98.9	0.55	682.0	1.62	8639	0.47	2130	1.20	193.0
	45	56.0	11523	1.07	0.28	0.76	5.64	74.6	19535	2908	355.0	0.46	565.0	1.20	6495	0.45	2371	0.81	240.9
Average		94.5	14699	1.05	0.30	0.90	4.79	108.1	18204	3974	182.1	0.45	684.2	1.20	6436	0.63	2151	1.72	154.7
Std dev		59.4	3100	0.33	0.03	0.12	1.05	49.9	1280	976	149.8	0.10	120.3	0.42	2233	0.29	210	1.26	110.4
1st stems	15	20.7	2288	0.47	0.04	0.05	3.06	112.4	3541	651	7.8	0.07	14.5	0.21	899	0.14	430	1.08	27.06
15/10/2007	20	16.9	2184	0.42	0.04	0.01	2.52	35.1	3431	634	4.8	0.03	12.1	0.17	964	0.16	417	0.10	27.86
	45	21.5	2160	0.68	0.01	0.03	4.17	48.3	4164	604	29.2	0.00	11.8	0.29	1140	0.11	495	0.10	77.06
Average		19.7	2211	0.52	0.03	0.03	3.25	65.3	3712	630	13.9	0.03	12.8	0.22	1001	0.14	448	0.42	44.0
Std dev		2.5	68	0.14	0.02	0.02	0.84	41.4	395	24	13.3	0.04	1.5	0.06	125	0.03	42	0.57	28.6
2nd stems	15	15.7	2545	0.63	0.00	0.30	3.06	23.3	3172	718	7.8	0.01	35.0	0.60	1000	1.56	471	0.45	41.80
11/03/2008	20	20.2	2490	0.45	-0.01	0.05	2.46	15.1	3048	705	5.9	0.01	37.9	0.13	1028	0.04	455	0.40	32.70
	45	25.9	2340	0.82	-0.02	0.13	4.26	36.9	2691	666	29.0	0.01	33.4	0.26	1072	0.46	520	0.85	74.61
Average		20.6	2458	0.63	-0.01	0.16	3.26	25.1	2970	697	14.2	0.01	35.4	0.33	1034	0.69	482	0.57	49.7
Std dev		5.1	106	0.18	0.01	0.13	0.92	11.0	250	27	12.9	0.00	2.3	0.24	36	0.79	34	0.25	22.0
3rd stems	15	7.7	2436	0.37	0.02	0.09	2.56	17.7	2512	610	8.2	0.05	3.5	0.17	861	-0.65	285	0.16	46.85
30/09/2008	20	7.7	2210	0.44	0.01	-0.26	2.39	15.8	2324	571	15.4	0.04	5.3	0.11	810	-1.10	272	0.08	53.67
	45	10.5	2442	1.04	0.02	-0.38	2.69	13.8	2726	582	48.1	0.01	21.5	0.21	895	0.51	331	0.06	105.21
Average		8.6	2363	0.62	0.02	-0.18	2.55	15.7	2521	588	23.9	0.03	10.1	0.16	855	-0.41	296	0.10	68.6
Std dev		1.6	133	0.37	0.01	0.24	0.15	2.0	201	20	21.3	0.02	9.9	0.05	43	0.83	31	0.05	31.9
4th stems	15	5.1	2509	0.74	-0.03	-0.38	2.63	8.9	2413	640	8.0	-0.22	13.1	0.05	837	-0.25	313	0.00	29.29
08/12/2003	20	9.6	2879	0.69	-0.03	-0.40	2.62	12.2	2548	665	21.5	-0.23	25.9	0.07	891	-0.34	341	0.00	68.82
	45	8.8	2578	0.61	-0.15	-0.43	2.84	13.4	2881	632	60.0	-0.29	36.7	-0.07	911	-0.33	383	0.00	105.84
Average		7.8	2655	0.68	-0.07	-0.40	2.70	11.5	2614	646	29.8	-0.25	25.2	0.02	880	-0.30	345	0.00	68.0
Std dev		2.4	196	0.07	0.07	0.03	0.13	2.3	241	17	26.9	0.04	11.8	0.08	38	0.05	35	0.00	38.3
5th stems	15	8.8	3832	0.52	0.00	0.57	3.25	15.0	2697	698	14.05	0.00	20.3	0.00	812	0.34	280	0.00	44.31
12/10/2009	20	2.7	2440	0.58	0.00	0.46	2.55	7.5	1957	603	11.00	0.00	4.8	0.01	796	0.21	231	0.00	55.61
	45	8.2	2561	0.79	0.16	0.63	3.83	11.8	2341	649	36.37	0.00	10.3	0.06	902	0.32	283	0.00	77.31
Average		6.5	2945	0.63	0.05	0.55	3.21	11.5	2332	650	20.5	0.00	11.8	0.02	837	0.29	265	0.00	59.1
Std dev		3.4	771	0.14	0.09	0.09	0.64	3.8	370	48	13.9	0.00	7.8	0.03	58	0.07	29	0.00	16.8
6th stems	15	8.2	2448	0.64	0.00	0.00	2.45	4.6	1886	576	7.51	0.00	17.0	0.00	756	0.00	227	0.00	50.28
18/01/2010	20	8.6	2668	0.71	0.00	0.00	2.89	9.5	2308	632	6.46	0.00	13.8	0.00	923	0.00	266	0.00	61.52
	45	7.3	1947	0.85	0.00	0.00	2.04	6.6	2366	492	43.24	0.00	18.3	0.00	767	0.00	231	0.00	81.65
Average		8.0	2354	0.73	0.00	0.00	2.46	6.9	2186	567	19.1	0.00	16.4	0.00	815	0.00	241	0.00	64.5
Std dev		0.7	370	0.11	0.00	0.00	0.43	2.5	262	70	20.9	0.00	2.3	0.00	93	0.00	21	0.00	15.9

Table C6 Metal content in SRC Willow raw fuel for Treatment O (Sewage) Pellets

Sampling	Plot	Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Ti	Zn
1st leaves	8	49.5	9171	0.95	0.18	0.20	4.55	72.5	18164	2417	79.5	0.51	473.5	0.81	2719	0.25	3255	4.56	89.6
15/10/2007	17	55.9	10355	0.94	0.12	0.24	6.85	91.1	21269	2525	51.4	0.60	354.7	1.33	3808	0.37	3985	1.61	107.9
	31	54.9	9757	1.38	0.23	0.28	5.75	81.2	25912	2525	60.1	0.38	612.1	1.57	3569	0.42	3012	1.80	115.1
Average		53.5	9761	1.09	0.18	0.24	5.72	81.6	21782	2489	63.7	0.49	480.1	1.24	3365	0.35	3417	2.66	104.2
Std dev		3.4	592	0.25	0.05	0.04	1.15	9.3	3899	62	14.4	0.11	128.9	0.39	572	0.09	506	1.65	13.1
3rd leaves	8	67.3	15407	1.96	0.29	-0.05	9.06	127.6	17260	3338	178.3	0.55	330.4	3.51	7664	0.97	3105	2.01	477.8
30/09/2008	17	57.9	13316	0.80	0.18	-0.29	7.57	100.9	18690	3186	50.1	0.66	385.0	2.72	5104	1.06	3459	1.58	191.5
	31	61.2	13553	1.46	0.33	-0.32	8.23	106.9	18221	3378	113.5	0.49	434.2	2.37	6143	1.17	3307	1.47	367.2
Average		62.1	14092	1.41	0.27	-0.22	8.29	111.8	18057	3300	114.0	0.57	383.2	2.87	6303	1.07	3291	1.69	345.5
Std dev		4.8	1145	0.59	0.08	0.15	0.75	14.0	729	101	64.1	0.08	51.9	0.58	1288	0.10	178	0.28	144.4
5th leaves	8	49.9	15852	1.45	0.32	0.83	5.11	64.2	16414	3746	118.8	0.73	625.8	1.30	7704	0.29	2723	0.69	254.6
12/10/2009	17	54.7	18768	1.46	0.19	0.80	5.67	70.2	16181	4224	69.2	1.02	611.6	1.70	7131	0.06	3398	0.84	304.3
	31	51.0	14365	1.60	0.25	0.70	4.85	70.8	13030	3585	99.6	0.50	516.0	1.00	5099	0.17	1765	0.81	318.8
Average		51.9	16328	1.51	0.25	0.78	5.21	68.4	15208	3851	95.9	0.75	584.5	1.33	6645	0.17	2629	0.78	292.6
Std dev		2.5	2240	0.08	0.06	0.07	0.42	3.6	1890	332	25.0	0.26	59.7	0.35	1369	0.12	820	0.08	33.7
1st stems	8	10.5	2208	0.50	0.03	0.00	3.14	32.7	3564	644	19.1	0.04	11.9	0.16	968	0.06	421	0.06	63.24
15/10/2007	17	8.0	1993	0.44	0.03	0.01	3.05	47.3	3158	614	7.9	0.04	17.2	0.17	910	0.04	408	0.07	55.41
	31	20.7	2189	0.63	0.02	0.02	3.22	37.5	3133	641	12.3	0.00	9.1	0.17	951	0.25	411	0.04	60.69
Average		13.0	2130	0.52	0.03	0.01	3.14	39.2	3285	633	13.1	0.03	12.7	0.17	943	0.11	413	0.06	59.8
Std dev		6.7	119	0.10	0.01	0.01	0.09	7.5	242	16	5.7	0.02	4.1	0.01	30	0.12	7	0.01	4.0
2nd stems	8	6.0	2323	0.59	0.02	0.03	2.88	17.0	2730	688	16.1	0.03	28.5	0.16	878	0.12	407	0.00	61.30
11/03/2008	17	10.8	2454	0.44	0.00	0.03	2.88	17.3	2598	645	8.3	0.04	25.4	0.07	833	0.10	432	0.40	54.15
	31	18.3	2612	0.70	0.01	0.14	3.21	33.9	2873	723	17.6	0.02	42.2	0.21	1006	0.10	492	0.41	76.04
Average		11.7	2463	0.58	0.01	0.07	2.99	22.7	2734	686	14.0	0.03	32.0	0.15	906	0.10	444	0.27	63.8
Std dev		6.2	144	0.13	0.01	0.06	0.19	9.7	138	39	5.0	0.01	8.9	0.07	90	0.01	44	0.23	11.2
3rd stems	8	7.2	2614	1.12	0.00	0.04	3.61	22.0	2685	666	22.3	0.03	0.8	0.15	1019	0.00	348	0.11	115.98
30/09/2008	17	5.3	2424	0.25	0.00	0.00	2.40	13.3	2542	568	7.6	0.07	5.0	0.18	838	0.00	321	0.07	70.45
	31	8.3	2211	0.55	0.02	0.00	2.49	11.6	2113	563	14.1	0.03	8.5	0.11	809	0.00	285	0.06	90.39
Average		6.9	2416	0.64	0.01	0.01	2.83	15.7	2447	599	14.7	0.04	4.8	0.14	888	0.00	318	0.08	92.3
Std dev		1.5	201	0.44	0.01	0.02	0.67	5.6	298	58	7.4	0.02	3.9	0.03	114	0.00	32	0.03	22.8
4th stems	8	9.9	3493	1.25	0.00	0.00	4.88	16.7	3156	806	31.0	0.00	35.3	0.18	1114	0.00	449	0.00	159.84
08/12/2003	17	9.2	2700	0.61	0.03	0.00	3.48	16.6	2834	605	11.5	0.11	27.0	0.19	886	0.00	421	0.11	87.53
	31	9.6	2213	0.64	0.00	0.00	2.80	12.6	2235	580	15.9	0.00	23.3	0.01	816	0.05	323	0.09	85.69
Average		9.5	2802	0.83	0.01	0.00	3.72	15.3	2742	664	19.4	0.04	28.5	0.13	939	0.02	398	0.07	111.0
Std dev		0.4	646	0.36	0.02	0.00	1.06	2.4	468	124	10.2	0.06	6.2	0.10	155	0.03	66	0.06	42.3
5th stems	8	9.3	2498	0.63	0.00	0.39	2.76	15.9	2059	582	12.63	0.00	4.3	0.02	784	0.30	246	0.00	86.66
12/10/2009	17	9.1	2651	0.66	0.03	0.56	2.94	12.7	2570	595	7.33	0.16	14.4	0.18	844	0.35	297	0.07	83.36
	31	15.0	2577	0.77	0.00	0.33	2.35	11.1	2132	630	9.97	0.00	6.5	0.06	845	0.19	277	0.03	79.68
Average		11.1	2575	0.69	0.01	0.43	2.68	13.2	2254	602	10.0	0.05	8.4	0.09	824	0.28	273	0.04	83.2
Std dev		3.4	76	0.07	0.02	0.12	0.30	2.5	276	25	2.7	0.09	5.3	0.09	35	0.08	25	0.04	3.5
6th stems	8	3.5	2588	0.95	0.00	0.00	2.77	5.6	2260	593	10.57	0.00	13.7	0.02	841	0.00	277	0.00	96.01
18/01/2010	17	12.5	2972	0.68	0.00	0.00	3.21	14.7	2836	619	5.38	0.09	34.1	0.17	952	0.00	332	0.22	80.37
	31	10.5	2648	0.91	0.00	0.00	3.41	19.5	2364	650	10.52	0.02	23.7	0.05	942	0.00	318	0.04	98.46
Average		8.9	2736	0.85	0.00	0.00	3.13	13.3	2486	621	8.8	0.03	23.8	0.08	912	0.00	309	0.09	91.6
Std dev		4.7	207	0.15	0.00	0.00	0.33	7.0	307	29	3.0	0.05	10.2	0.08	61	0.00	29	0.11	9.8

APPENDIX D: Calculated Ash Composition and Slagging and Fouling Indices of SRC Willow

Table D1 Calculated Ash Composition and Slagging and Fouling Indices for SRC Willow for Treatment A (0 Kg N)

		% in ash											Kg alkali/GJ	
Sampling	**Plot**	**Al_2O_3**	**CaO**	**Fe_2O_3**	**K_2O**	**MgO**	**Mn_3O_4**	**Na_2O**	**P_2O_5**	**SO_3**	**TiO_2**	**Total**	**AI**	**Base %**
1st leaves	7	0.20	25.2	0.23	43.3	8.17	0.12	0.94	20.5	10.58	0.0063	109	1.28	77.9
15/10/2007	21	0.35	31.1	0.32	32.5	10.17	0.11	0.91	19.3	9.69	0.0089	104	1.02	75.0
	44	0.22	19.9	0.28	42.8	5.43	0.34	1.40	16.7	8.95	0.0069	96	1.33	69.8
Average		0.26	25.4	0.28	39.5	7.92	0.19	1.08	18.9	9.74	0.0073	103	1.21	74.2
Std dev		0.08	5.6	0.04	6.1	2.38	0.13	0.28	1.9	0.82	0.0014	7	0.17	4.1
3rd leaves	7	0.12	28.3	0.16	28.4	8.93	0.18	0.62	32.9	9.18	0.0025	109	1.06	66.5
30/09/2008	21	0.11	35.8	0.16	23.1	10.63	0.19	0.43	31.3	8.57	0.0028	110	0.84	70.2
	44	0.17	19.8	0.21	32.0	6.24	0.93	0.62	24.0	8.87	0.0032	93	1.17	58.8
Average		0.13	28.0	0.18	27.8	8.60	0.43	0.56	29.4	8.87	0.0028	104	1.03	65.2
Std dev		0.04	8.0	0.03	4.4	2.22	0.43	0.11	4.8	0.31	0.0003	10	0.17	5.8
5th leaves	7	0.12	31.9	0.12	19.8	10.94	0.10	1.17	29.2	11.79	0.0021	105	0.87	63.9
12/10/2009	21	0.10	35.9	0.10	18.6	10.86	0.12	0.76	29.1	6.64	0.0012	102	0.86	66.2
	44	0.16	28.5	0.16	23.3	8.63	1.07	1.33	20.5	13.02	0.0019	97	0.99	61.9
Average		0.13	32.1	0.13	20.6	10.14	0.43	1.09	26.3	10.48	0.0017	101	0.91	64.0
Std dev		0.03	3.7	0.03	2.4	1.31	0.55	0.29	5.0	3.38	0.0005	4	0.07	2.2
1st stems	7	0.10	15.1	0.20	18.5	5.02	0.07	0.06	10.0	4.14	0.0005	53	0.206	38.9
15/10/2007	21	0.13	14.1	0.34	17.6	4.74	0.05	0.01	9.3	3.53	0.0006	50	0.193	36.8
	44	0.26	39.9	0.62	48.2	13.37	0.60	0.14	30.1	13.57	0.0010	147	0.189	102.2
Average		0.16	23.0	0.39	28.1	7.71	0.24	0.07	16.5	7.080	0.001	83	0.20	59.3
Std dev		0.08	14.6	0.21	17.4	4.91	0.31	0.07	11.8	5.63	0.00	55	0.01	37.2
2nd stems	7	0.07	16.6	0.10	18.4	5.80	0.10	0.16	11.0	4.75	0.0000	57	0.180	41.0
11/03/2008	21	0.19	14.9	0.08	16.2	5.20	0.06	0.11	10.5	3.94	0.0027	51	0.168	36.5
	44	0.27	41.4	0.30	43.3	13.91	1.46	0.62	32.6	13.19	0.0061	147	0.186	99.5
Average		0.18	24.3	0.16	26.0	8.30	0.54	0.29	18.0	7.295	0.003	85	0.178	59.0
Std dev		0.10	14.8	0.12	15.0	4.87	0.80	0.28	12.6	5.12	0.00	54	0.01	35.1
3rd stems	7	0.19	38.4	0.25	35.4	13.00	0.17	0.00	19.5	9.53	0.0006	116	0.174	87.1
30/09/2008	21	0.21	55.9	0.49	39.7	17.22	0.21	0.11	25.4	12.04	0.0022	151	0.145	113.5
	44	0.20	39.8	0.27	39.7	12.31	1.18	0.34	19.8	9.58	0.0021	123	0.182	92.4
Average		0.20	44.7	0.33	38.3	14.17	0.52	0.15	21.6	######	0.0016	130	0.167	97.6
Std dev		0.01	9.7	0.14	2.5	2.66	0.57	0.17	3.3	1.43	0.00	19	0.02	14.0
4th stems	7	0.07	24.4	0.11	21.0	8.26	0.09	0.17	17.1	6.21	0.0000	77	0.143	54.0
08/12/2003	21	0.11	30.7	0.12	21.0	9.42	0.12	0.23	16.1	6.69	0.0000	85	0.163	61.5
	44	0.17	24.2	0.16	25.4	8.14	0.93	0.26	17.7	6.91	0.0083	84	0.171	58.2
Average		0.12	26.4	0.13	22.5	8.61	0.38	0.22	17.0	6.603	0.003	82	0.159	57.9
Std dev		0.07	0.2	0.04	3.1	0.09	0.60	0.06	0.4	0.49	0.01	5	0.02	3.0
5th stems	7	0.11	40.9	0.13	32.3	13.81	0.10	0.08	25.7	8.21	0.0000	121	0.148	87.2
12/10/2009	21	0.11	41.4	0.12	23.5	11.42	0.09	0.07	19.9	6.55	0.0000	103	0.165	76.5
	44	0.24	35.6	0.21	32.1	10.99	0.72	0.20	23.4	8.43	0.0003	112	0.196	79.2
Average		0.15	39.3	0.15	29.3	12.07	0.30	0.12	23.0	7.73	0.00	112	0.17	81.0
Std dev		0.09	3.7	0.05	0.1	1.99	0.44	0.08	1.6	0.16	0.00	7	0.03	5.7
6th stems	7	0.13	35.5	0.08	28.6	10.78	0.08	0.20	21.5	7.63	0.0000	105	0.158	75.3
18/01/2010	21	0.18	33.4	0.16	25.7	10.15	0.08	0.27	20.5	7.11	0.0000	98	0.156	69.7
	44	0.31	35.1	0.15	28.1	11.24	0.09	0.32	22.7	6.98	0.0000	105	0.142	74.9
Average		0.21	34.7	0.13	27.5	10.72	0.08	0.26	21.6	7.24	0.00	102	0.15	73.3
Std dev		0.12	0.3	0.05	0.4	0.32	0.00	0.08	0.9	0.46	0.00	0	0.01	0.2

Table D2 Calculated Ash Composition and Slagging and Fouling Indices for SRC Willow for Treatment D (150 Kg N)

		% in ash											Kg alkali/GJ	
Sampling	**Plot**	**Al_2O_3**	**CaO**	**Fe_2O_3**	**K_2O**	**MgO**	**Mn_3O_4**	**Na_2O**	**P_2O_5**	**SO_3**	**TiO_2**	**Total**	**AI**	**Base %**
1st leaves	14	0.29	24.4	0.32	44.5	7.46	0.14	0.93	12.9	7.46	0.0090	98	1.52	77.6
15/10/2007	16	0.23	28.6	0.22	35.4	8.67	0.06	0.77	16.3	9.93	0.0055	100	1.16	73.7
	32	0.13	22.1	0.16	37.7	7.32	0.06	1.07	7.5	6.45	0.0038	83	1.17	68.4
Average		0.22	25.0	0.23	39.2	7.82	0.09	0.92	12.3	7.95	0.0061	94	1.28	73.2
Std dev		0.08	3.3	0.08	4.7	0.74	0.05	0.15	4.4	1.79	0.0027	10	0.20	4.6
3rd leaves	14	0.30	37.2	0.32	41.0	11.69	0.33	1.09	27.4	12.42	0.0064	132	1.51	91.3
30/09/2008	16	0.29	39.2	0.33	42.2	12.65	0.09	0.69	22.0	17.63	0.0073	135	1.63	95.0
	32	0.19	30.7	0.26	39.8	9.98	0.14	0.83	21.3	12.56	0.0049	116	1.35	81.6
Average		0.26	35.7	0.30	41.0	11.44	0.18	0.87	23.6	14.20	0.0062	128	1.50	89.3
Std dev		0.06	4.4	0.04	1.2	1.35	0.12	0.20	3.4	2.97	0.0012	10	0.14	6.9
5th leaves	14	0.13	24.7	0.13	26.1	6.57	0.15	1.53	17.0	6.46	0.0022	83	1.22	59.0
12/10/2009	16	0.13	37.4	0.14	16.6	10.23	0.09	0.97	23.2	9.84	0.0019	99	0.79	65.3
	32	0.13	26.4	0.13	29.5	8.02	0.10	1.20	15.0	7.11	0.0017	88	1.22	65.2
Average		0.13	29.5	0.13	24.1	8.27	0.11	1.23	18.4	7.80	0.0020	90	1.08	63.2
Std dev		0.00	6.9	0.00	6.7	1.85	0.03	0.28	4.2	1.79	0.0002	8	0.25	3.6
1st stems	14	0.21	34.6	1.29	53.3	12.80	0.19	0.23	29.4	11.28	0.0127	143	0.26	102.2
15/10/2007	16	0.20	28.9	0.33	38.9	9.55	0.05	0.21	21.4	9.64	0.0011	109	0.21	77.9
	32	0.74	46.2	1.01	58.8	16.45	0.12	0.17	34.6	15.58	0.0019	174	0.21	122.6
Average		0.38	36.5	0.88	50.3	12.93	0.12	0.20	28.5	12.16	0.005	142	0.22	100.9
Std dev		0.31	8.8	0.49	10.3	3.45	0.07	0.03	6.7	3.07	0.01	32	0.03	22.4
2nd stems	14	3.03	20.7	6.40	15.1	4.14	0.17	0.30	9.1	5.78	0.0579	65	0.19	46.6
11/03/2008	16	0.21	29.3	0.21	30.8	9.44	0.06	0.38	19.5	9.96	0.0046	100	0.17	70.1
	32	0.67	54.5	1.33	47.2	17.30	0.13	0.71	28.2	15.08	0.0327	165	0.16	121.0
Average		1.31	34.8	2.65	31.0	10.29	0.12	0.46	18.9	10.272	0.032	110	0.17	79.2
Std dev		1.51	17.6	3.30	16.0	6.62	0.05	0.22	9.6	4.66	0.03	51	0.01	38.0
3rd stems	14	0.11	30.3	0.17	25.9	9.35	0.19	0.04	13.9	6.37	0.0028	86	0.14	65.8
30/09/2008	16	0.27	66.4	0.87	64.0	18.13	0.13	0.17	29.7	16.49	0.0058	196	0.17	149.6
	32	0.16	32.3	0.17	27.8	9.57	0.10	0.12	13.2	7.24	0.0012	91	0.16	69.9
Average		0.18	43.0	0.40	39.2	12.35	0.14	0.11	18.9	10.03	0.0033	124	0.16	95.1
Std dev		0.08	20.3	0.40	21.5	5.00	0.05	0.07	9.3	5.61	0.00	62	0.02	47.2
4th stems	14	0.06	26.4	0.12	24.1	7.76	0.13	0.25	15.1	5.68	0.0000	80	0.15	58.6
08/12/2003	16	0.09	25.5	0.10	22.2	6.99	0.06	0.20	13.7	6.39	0.0000	75	0.16	55.0
	32	0.06	27.9	0.12	24.5	8.35	0.09	0.23	15.5	6.84	0.0000	84	0.16	61.1
Average		0.07	26.6	0.11	23.6	7.70	0.09	0.22	14.8	6.31	0.000	80	0.16	58.3
Std dev		0.00	1.0	0.00	0.3	0.42	0.03	0.01	0.3	0.82	0.00	3	0.00	1.8
5th stems	14	0.13	48.2	0.19	32.7	13.69	0.20	0.12	25.2	7.99	0.0000	128	0.14	95.0
12/10/2009	16	0.15	43.2	0.13	30.3	11.20	0.08	0.18	20.5	7.84	0.0000	114	0.19	85.1
	32	0.28	37.0	0.20	27.6	10.70	0.09	0.19	19.5	6.86	0.0031	102	0.16	75.7
Average		0.18	42.8	0.18	30.2	11.86	0.12	0.17	21.7	7.57	0.00	115	0.16	85.2
Std dev		0.09	5.6	0.04	2.6	1.60	0.07	0.04	3.0	0.62	0.00	13	0.02	9.6
6th stems	14	0.13	37.5	0.08	30.9	11.30	0.21	0.23	22.8	7.55	0.0000	111	0.14	80.0
18/01/2010	16	0.10	35.6	0.10	30.1	10.52	0.07	0.22	20.6	7.42	0.0000	105	0.15	76.5
	32	0.10	35.1	0.10	26.0	10.16	0.09	0.26	19.0	6.68	0.0000	98	0.16	71.6
Average		0.11	36.1	0.09	29.0	10.66	0.12	0.24	20.8	7.21	0.00	104	0.15	76.0
Std dev		0.02	1.3	0.01	2.6	0.58	0.08	0.02	1.9	0.47	0.00	7	0.01	4.2

Table D3 Calculated Ash Composition and Slagging and Fouling Indices for SRC Willow for Treatment F (250 Kg N)

		% in ash											Kg alkali/GJ	
Sampling	Plot	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Mn_3O_4	Na_2O	P_2O_5	SO_3	TiO_2	Total	AI	Base %
1st leaves	6	0.16	23.5	0.19	36.4	7.08	0.08	0.73	13.9	6.93	0.0038	89	0.95	67.9
15/10/2007	26	0.19	30.7	0.23	29.9	10.00	0.09	0.93	14.1	9.30	0.0061	95	1.01	71.8
	36	0.12	20.6	0.15	39.5	7.06	0.07	0.90	8.7	6.64	0.0029	84	1.37	68.1
Average		0.16	24.9	0.19	35.2	8.05	0.08	0.85	12.2	7.62	0.0042	89	1.11	69.3
Std dev		0.03	5.2	0.04	4.9	1.69	0.01	0.11	3.0	1.46	0.0017	6	0.23	2.2
3rd leaves	6	0.10	26.8	0.16	30.6	6.32	0.10	0.30	15.5	14.66	0.0026	95	1.39	64.2
30/09/2008	26	0.11	29.8	0.18	25.2	9.96	0.09	0.48	18.4	10.73	0.0027	95	1.06	65.6
	36	0.14	24.3	0.21	29.1	6.94	0.07	0.77	12.8	11.70	0.0037	86	1.09	61.3
Average		0.12	27.0	0.18	28.3	7.74	0.08	0.51	15.6	12.36	0.0030	92	1.18	63.7
Std dev		0.02	2.8	0.02	2.8	1.95	0.02	0.24	2.8	2.05	0.0006	5	0.18	2.2
5th leaves	6	0.09	35.7	0.10	19.6	10.10	0.13	1.01	20.6	12.23	0.0009	100	0.90	66.5
12/10/2009	26	0.15	28.6	0.16	24.2	8.98	0.10	1.18	16.1	6.55	0.0024	86	0.95	63.1
	36	0.15	27.8	0.17	31.4	9.22	0.20	1.50	15.5	11.65	0.0023	98	1.11	70.1
Average		0.13	30.7	0.14	25.1	9.43	0.14	1.23	17.4	10.14	0.0019	94	0.99	66.6
Std dev		0.03	4.3	0.04	5.9	0.59	0.05	0.25	2.8	3.12	0.0008	7	0.11	3.5
1st stems	6	0.13	31.8	0.45	49.6	10.90	0.10	0.21	28.6	11.98	0.0011	134	0.23	92.9
15/10/2007	26	0.25	28.1	0.77	34.9	9.04	0.07	0.15	19.9	8.56	0.0013	102	0.20	73.0
	36	0.36	23.3	0.33	34.9	8.73	0.07	0.11	19.0	8.92	0.0003	96	0.23	67.4
Average		0.25	27.7	0.52	39.8	9.55	0.08	0.15	22.5	9.82	0.001	110	0.22	77.8
Std dev		0.11	4.3	0.23	8.4	1.17	0.02	0.05	5.3	1.88	0.00	20	0.02	13.4
2nd stems	6	0.38	56.0	0.41	61.5	17.86	0.17	0.81	39.7	19.61	0.0000	196	0.23	136.6
11/03/2008	26	0.36	58.5	0.35	54.1	19.37	0.11	1.21	35.8	17.93	0.0121	188	0.19	133.5
	36	0.28	35.3	0.26	31.9	11.55	0.06	0.42	21.5	11.26	0.0060	113	0.16	79.4
Average		0.34	49.9	0.34	49.2	16.26	0.11	0.81	32.3	16.270	0.006	166	0.19	116.5
Std dev		0.05	12.8	0.08	15.4	4.15	0.06	0.40	9.6	4.42	0.01	46	0.03	32.1
3rd stems	6	0.20	36.9	0.50	30.5	9.91	0.11	0.01	23.0	9.64	0.0039	111	0.21	77.8
30/09/2008	26	0.17	32.0	0.41	27.3	9.37	0.08	0.18	16.9	7.23	0.0020	94	0.18	69.2
	36	0.17	26.4	0.19	21.5	8.32	0.09	0.12	16.1	6.19	0.0009	79	0.15	56.5
Average		0.18	31.7	0.37	26.4	9.20	0.09	0.10	18.7	7.69	0.0022	94	0.18	67.8
Std dev		0.01	5.3	0.16	4.6	0.81	0.02	0.09	3.8	1.77	0.00	16	0.03	10.7
4th stems	6	0.12	25.8	0.12	23.6	7.32	0.11	0.18	16.1	7.44	0.0000	81	0.16	57.0
08/12/2003	26	0.11	29.2	0.09	25.1	8.49	0.06	0.25	15.5	6.86	0.0000	86	0.17	63.2
	36	0.11	25.4	0.11	23.7	7.65	0.06	0.24	13.5	6.35	0.0000	77	0.18	57.1
Average		0.12	26.8	0.11	24.1	7.82	0.08	0.22	15.1	6.88	0.000	81	0.17	59.1
Std dev		0.00	0.2	0.01	0.1	0.24	0.03	0.04	1.9	0.77	0.00	3	0.01	0.1
5th stems	6	0.09	36.8	0.12	27.6	9.79	0.10	0.07	18.2	6.96	0.0000	100	0.14	74.4
12/10/2009	26	0.23	45.0	0.21	29.9	12.71	0.09	0.19	20.8	7.49	0.0014	117	0.15	88.0
	36	0.29	58.4	0.25	42.7	16.55	0.19	0.26	29.7	10.94	0.0010	159	0.16	118.2
Average		0.20	46.8	0.19	33.4	13.02	0.13	0.17	22.9	8.46	0.00	125	0.15	93.5
Std dev		0.14	15.3	0.09	10.7	4.77	0.06	0.13	8.1	2.82	0.00	42	0.01	31.0
6th stems	6	0.30	44.7	0.24	35.0	12.32	0.12	0.43	23.0	9.32	0.0005	125	0.16	92.8
18/01/2010	26	0.19	54.4	0.19	33.3	12.19	0.10	0.45	21.7	7.93	0.0000	130	0.18	100.5
	36	0.17	46.9	0.24	36.6	11.77	0.09	0.40	23.7	8.88	0.0000	129	0.18	95.9
Average		0.22	48.7	0.22	35.0	12.09	0.10	0.42	22.8	8.71	0.00	128	0.17	96.4
Std dev		0.10	1.5	0.01	1.1	0.39	0.02	0.02	0.5	0.31	0.00	2	0.01	2.2

Table D4 Calculated Ash Composition and Slagging and Fouling Indices for SRC Willow for Treatment J (150 Kg N + 100Kg K)

		% in ash											Kg alkali/GJ	
Sampling	Plot	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Mn_3O_4	Na_2O	P_2O_5	SO_3	TiO_2	Total	AI	Base %
1st leaves	12	0.20	24.8	0.23	46.7	7.13	0.07	0.89	12.7	10.98	0.0057	104	1.38	79.8
15/10/2007	24	0.19	22.1	0.21	43.1	5.83	0.20	0.80	12.7	7.87	0.0059	93	1.42	72.0
	39	0.19	24.0	0.24	37.4	8.91	0.18	1.18	11.6	6.20	0.0057	90	1.19	71.8
Average		0.19	23.6	0.23	42.4	7.29	0.15	0.96	12.4	8.35	0.0058	96	1.33	74.5
Std dev		0.01	1.4	0.02	4.7	1.54	0.07	0.20	0.6	2.43	0.0001	7	0.12	4.5
3rd leaves	12	0.10	22.1	0.18	34.2	7.53	0.07	0.51	14.6	13.52	0.0026	93	1.22	64.5
30/09/2008	24	0.20	23.7	0.25	32.9	6.68	0.41	0.82	18.9	9.15	0.0045	93	1.22	64.3
	39	0.11	22.5	0.17	29.8	6.32	0.34	0.71	17.3	8.16	0.0026	85	1.03	59.5
Average		0.14	22.7	0.20	32.3	6.85	0.27	0.68	16.9	10.28	0.0032	90	1.16	62.8
Std dev		0.06	0.8	0.05	2.2	0.62	0.18	0.16	2.2	2.85	0.0011	4	0.11	2.9
5th leaves	12	0.09	24.6	0.11	35.0	7.16	0.08	1.00	17.1	9.04	0.0012	94	1.44	67.9
12/10/2009	24	0.11	30.4	0.12	23.5	8.12	0.28	0.85	20.7	9.83	0.0019	94	0.95	63.1
	39	0.11	33.7	0.13	26.4	9.60	0.26	0.99	28.1	9.05	0.0009	108	1.03	70.8
Average		0.10	29.6	0.12	28.3	8.30	0.21	0.94	22.0	9.31	0.0013	99	1.14	67.3
Std dev		0.01	4.6	0.01	6.0	1.23	0.11	0.08	5.6	0.45	0.0005	8	0.26	3.9
1st stems	12	0.16	33.0	0.56	48.5	11.98	0.08	0.25	25.9	12.14	0.0012	133	0.23	94.3
15/10/2007	24	0.23	29.6	0.41	46.0	9.94	0.26	0.19	23.5	9.97	0.0031	120	0.25	86.1
	39	0.55	32.3	0.44	43.6	11.32	0.23	0.09	24.7	8.90	0.0000	122	0.20	87.7
Average		0.31	31.6	0.47	46.0	11.08	0.19	0.18	24.7	10.34	0.001	125	0.23	89.4
Std dev		0.21	1.8	0.08	2.4	1.04	0.10	0.08	1.2	1.65	0.00	7	0.02	4.3
2nd stems	12	0.83	69.0	0.69	65.5	23.06	0.17	0.81	44.4	23.77	0.0159	228	0.18	159.0
11/03/2008	24	0.32	36.9	0.36	37.6	11.36	0.36	0.50	23.0	11.59	0.0052	122	0.21	86.7
	39	0.34	26.6	0.24	35.1	9.87	0.22	0.48	20.4	8.69	0.0058	102	0.21	72.2
Average		0.50	44.2	0.43	46.0	14.76	0.25	0.60	29.3	14.682	0.009	151	0.20	106.0
Std dev		0.29	22.1	0.24	16.9	7.22	0.10	0.19	13.2	8.00	0.01	68	0.02	46.5
3rd stems	12	0.15	31.7	0.21	35.1	9.77	0.07	0.03	14.5	9.33	0.0004	101	0.21	76.9
30/09/2008	24	0.17	28.7	0.23	27.7	7.59	0.32	0.11	12.1	6.47	0.0000	83	0.18	64.3
	39	0.09	26.1	0.17	26.3	7.76	0.30	0.11	11.3	6.36	0.0000	79	0.22	60.5
Average		0.13	28.9	0.20	29.7	8.38	0.23	0.09	12.6	7.39	0.0001	88	0.20	67.2
Std dev		0.04	2.8	0.03	4.7	1.21	0.14	0.05	1.6	1.68	0.00	12	0.02	8.6
4th stems	12	0.12	20.8	0.10	23.4	6.34	0.07	0.16	12.6	6.66	0.0000	70	0.18	50.9
08/12/2003	24	0.08	27.1	0.12	24.9	7.20	0.23	0.36	14.8	6.30	0.0000	81	0.18	59.8
	39	0.11	25.4	0.09	22.1	7.69	0.14	0.19	15.3	5.95	0.0000	77	0.19	55.5
Average		0.10	24.5	0.10	23.5	7.08	0.14	0.23	14.3	6.30	0.000	76	0.18	55.4
Std dev		0.01	3.2	0.01	0.9	0.96	0.05	0.02	1.9	0.50	0.00	5	0.01	3.3
5th stems	12	0.26	37.3	0.47	32.4	10.66	0.08	0.09	16.9	8.18	0.0000	106	0.15	80.9
12/10/2009	24	0.10	43.2	0.14	33.0	11.40	0.28	0.10	17.0	7.81	0.0000	113	0.17	87.8
	39	0.21	52.5	0.23	42.4	15.30	0.25	0.23	23.2	10.67	0.0004	145	0.22	110.6
Average		0.19	44.4	0.28	35.9	12.46	0.20	0.14	19.0	8.89	0.00	121	0.18	93.1
Std dev		0.08	7.7	0.17	5.6	2.49	0.11	0.08	3.6	1.56	0.00	21	0.04	15.5
6th stems	12	0.21	28.7	0.12	32.4	8.77	0.06	0.33	18.5	8.62	0.0000	98	0.17	70.3
18/01/2010	24	0.14	52.1	0.14	40.8	13.93	0.42	0.35	29.2	11.02	0.0000	148	0.15	107.3
	39	0.17	45.4	0.13	35.8	12.29	0.23	0.29	25.7	8.71	0.0000	129	0.15	94.0
Average		0.17	42.1	0.13	36.3	11.67	0.24	0.32	24.4	9.45	0.00	125	0.16	90.5
Std dev		0.03	11.8	0.00	2.4	2.49	0.12	0.03	5.1	0.07	0.00	22	0.01	16.7

Table D5 Calculated Ash Composition and Slagging and Fouling Indices for SRC Willow for Treatment N (150 Kg N + 80Kg S)

		% in ash											Kg alkali/GJ	
Sampling	Plot	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Mn_3O_4	Na_2O	P_2O_5	SO_3	TiO_2	Total	AI	Base %
1st leaves	15	0.14	18.4	0.17	47.7	5.08	0.06	0.99	6.8	9.43	0.0046	89	1.95	72.3
15/10/2007	20	0.17	24.3	0.19	41.0	7.28	0.06	1.07	10.7	11.34	0.0052	96	1.40	73.9
	45	0.17	21.8	0.23	39.4	5.48	0.30	0.89	10.8	12.99	0.0043	92	1.48	67.8
Average		0.16	21.5	0.20	42.7	5.95	0.14	0.98	9.5	11.25	0.0047	92	1.61	71.3
Std dev		0.02	3.0	0.03	4.4	1.17	0.14	0.09	2.3	1.78	0.0005	4	0.29	3.1
3rd leaves	15	0.12	28.4	0.17	28.0	9.43	0.13	0.70	18.9	10.61	0.0031	96	0.97	66.7
30/09/2008	20	0.13	26.8	0.18	30.4	8.44	0.30	0.86	21.8	9.77	0.0029	99	1.07	66.7
	45	0.14	19.5	0.18	32.5	6.31	0.60	0.72	17.6	9.65	0.0028	87	1.12	59.2
Average		0.13	24.9	0.18	30.3	8.06	0.34	0.76	19.4	10.01	0.0030	94	1.05	64.2
Std dev		0.01	4.7	0.01	2.3	1.60	0.24	0.08	2.1	0.52	0.0002	6	0.08	4.3
5th leaves	15	0.41	27.5	0.31	27.1	10.59	0.17	1.44	12.7	6.46	0.0070	87	1.03	67.0
12/10/2009	20	0.17	35.2	0.17	30.9	9.86	0.19	1.30	28.1	7.55	0.0029	113	1.18	77.4
	45	0.15	23.4	0.15	34.2	7.00	0.72	1.11	21.6	8.59	0.0020	97	1.31	65.8
Average		0.24	28.7	0.21	30.7	9.15	0.36	1.28	20.8	7.53	0.0039	99	1.17	70.1
Std dev		0.14	6.0	0.09	3.5	1.90	0.31	0.17	7.7	1.07	0.0027	13	0.14	6.4
1st stems	15	0.42	34.8	1.75	46.3	11.72	0.12	0.21	22.4	11.66	0.0196	129	0.24	94.8
15/10/2007	20	0.31	29.3	0.48	39.7	10.08	0.06	0.16	21.2	10.00	0.0015	111	0.20	79.7
	45	0.38	28.2	0.64	46.8	9.35	0.38	0.15	24.4	11.54	0.0015	122	0.24	85.2
Average		0.37	30.8	0.96	44.3	10.39	0.19	0.17	22.7	11.07	0.008	121	0.23	86.6
Std dev		0.06	3.5	0.69	4.0	1.21	0.17	0.03	1.6	0.93	0.01	9	0.02	7.6
2nd stems	15	0.39	43.1	0.69	42.7	14.53	0.53	0.59	32.3	17.08	0.0186	152	0.16	101.6
11/03/2008	20	0.51	45.5	0.34	40.4	13.49	0.15	0.06	26.3	9.48	0.0036	136	0.16	99.7
	45	0.48	30.3	0.22	27.4	9.29	0.21	0.07	18.2	6.66	0.0013	93	0.16	67.3
Average		0.46	39.6	0.42	36.8	12.44	0.30	0.24	25.6	11.074	0.008	127	0.16	89.5
Std dev		0.06	8.2	0.25	8.2	2.78	0.20	0.30	7.1	5.39	0.01	31	0.00	19.2
3rd stems	15	0.14	32.6	0.24	28.9	9.67	0.11	0.04	18.9	6.80	0.0026	97	0.16	71.5
30/09/2008	20	0.15	31.1	0.23	28.2	9.53	0.21	0.07	18.7	6.84	0.0013	95	0.15	69.1
	45	0.18	31.4	0.18	30.2	8.88	0.61	0.27	18.9	7.59	0.0009	98	0.17	71.0
Average		0.16	31.7	0.22	29.1	9.36	0.31	0.13	18.8	7.08	0.0016	97	0.16	70.5
Std dev		0.02	0.8	0.03	1.0	0.42	0.27	0.12	0.1	0.45	0.00	2	0.01	1.2
4th stems	15	0.08	28.9	0.10	23.9	8.72	0.09	0.15	15.8	6.42	0.0000	84	0.15	61.8
08/12/2003	20	0.14	31.0	0.13	23.6	8.48	0.23	0.27	15.7	6.54	0.0000	86	0.16	63.5
	45	0.12	27.0	0.14	26.0	7.85	0.62	0.37	15.6	7.15	0.0000	85	0.18	61.3
Average		0.11	29.0	0.13	24.5	8.35	0.31	0.26	15.7	6.70	0.000	85	0.16	62.2
Std dev		0.03	1.3	0.03	1.5	0.62	0.38	0.16	0.1	0.52	0.00	1	0.02	0.3
5th stems	15	0.21	68.7	0.28	41.7	14.84	0.25	0.35	23.8	8.98	0.0000	159	0.18	125.9
12/10/2009	20	0.07	46.8	0.15	32.3	13.69	0.21	0.09	25.0	7.92	0.0000	126	0.13	93.0
	45	0.19	43.2	0.20	34.0	12.96	0.61	0.17	24.9	8.51	0.0000	125	0.17	90.5
Average		0.16	52.9	0.21	36.0	13.83	0.36	0.20	24.6	8.47	0.00	137	0.16	103.1
Std dev		0.02	18.1	0.05	5.4	1.33	0.25	0.13	0.8	0.33	0.00	24	0.01	25.0
6th stems	15	0.23	50.4	0.10	33.4	14.05	0.15	0.34	25.5	8.34	0.0000	132	0.12	98.3
18/01/2010	20	0.17	39.3	0.14	29.3	11.04	0.09	0.20	22.3	6.99	0.0000	109	0.15	79.9
	45	0.13	26.7	0.09	27.9	8.00	0.59	0.24	17.2	5.65	0.0000	87	0.17	63.0
Average		0.18	38.8	0.11	30.2	11.03	0.28	0.26	21.7	6.99	0.00	109	0.15	80.4
Std dev		0.07	16.7	0.00	3.9	4.27	0.31	0.07	5.8	1.90	0.00	32	0.03	24.9

Table D6 Calculated Ash Composition and Slagging and Fouling Indices for SRC Willow for Treatment O (Sewage Pellets)

		% in ash											Kg alkali/GJ	
Sampling	**Plot**	**Al_2O_3**	**CaO**	**Fe_2O_3**	**K_2O**	**MgO**	**Mn_3O_4**	**Na_2O**	**P_2O_5**	**SO_3**	**TiO_2**	**Total**	**AI**	**Base %**
1st leaves	8	0.16	21.8	0.18	37.2	6.82	0.19	1.09	10.6	13.20	0.0124	91	1.16	67.1
15/10/2007	17	0.17	23.8	0.21	42.1	6.87	0.12	0.78	14.3	15.62	0.0042	104	1.61	73.7
	31	0.16	20.8	0.18	47.5	6.38	0.13	1.26	12.5	10.96	0.0044	100	1.84	76.1
Average		0.16	22.1	0.19	42.3	6.69	0.14	1.04	12.5	13.26	0.0070	98	1.54	72.3
Std dev		0.01	1.5	0.02	5.2	0.27	0.04	0.24	1.9	2.33	0.0047	6	0.35	4.7
3rd leaves	8	0.16	27.9	0.24	26.9	7.17	0.32	0.58	22.8	9.69	0.0042	96	1.07	62.9
30/09/2008	17	0.16	27.0	0.21	32.6	7.65	0.10	0.75	16.9	12.10	0.0037	98	1.13	68.2
	31	0.16	26.0	0.21	30.1	7.67	0.22	0.80	19.3	10.94	0.0033	95	1.48	64.7
Average		0.16	27.0	0.22	29.9	7.50	0.21	0.71	19.7	10.91	0.0037	96	1.23	65.3
Std dev		0.00	1.0	0.02	2.8	0.28	0.11	0.12	2.9	1.20	0.0005	1	0.22	2.7
5th leaves	8	0.13	31.5	0.13	28.0	8.81	0.23	1.20	25.0	9.04	0.0015	104	1.18	69.6
12/10/2009	17	0.14	35.0	0.13	26.0	9.34	0.13	1.10	21.8	10.63	0.0017	104	1.14	71.6
	31	0.15	30.7	0.15	24.0	9.09	0.21	1.06	17.9	6.33	0.0019	90	0.88	65.0
Average		0.14	32.4	0.14	26.0	9.08	0.19	1.12	21.6	8.67	0.0017	99	1.07	68.8
Std dev		0.01	2.3	0.01	2.0	0.26	0.06	0.07	3.6	2.17	0.0002	8	0.16	3.4
1st stems	8	0.23	35.5	0.54	49.4	12.27	0.31	0.18	25.5	12.09	0.0012	136	0.27	97.9
15/10/2007	17	0.27	49.4	1.20	67.5	18.06	0.19	0.41	37.0	18.09	0.0019	192	0.19	136.6
	31	0.41	31.8	0.56	39.2	11.03	0.18	0.13	22.6	10.64	0.0007	117	0.16	82.7
Average		0.30	38.9	0.76	52.0	13.79	0.23	0.24	28.4	13.61	0.001	148	0.20	105.7
Std dev		0.09	9.3	0.38	14.3	3.75	0.07	0.15	7.6	3.95	0.00	39	0.05	27.8
2nd stems	8	0.13	37.5	0.28	37.9	13.17	0.26	0.44	23.2	11.74	0.0000	125	0.16	89.3
11/03/2008	17	0.34	56.7	0.41	51.7	17.69	0.19	0.57	31.5	17.82	0.0109	177	0.18	127.1
	31	0.30	31.7	0.42	30.0	10.40	0.21	0.49	20.0	10.67	0.0059	104	0.19	73.1
Average		0.26	42.0	0.37	39.9	13.75	0.22	0.50	24.9	13.408	0.006	135	0.18	96.5
Std dev		0.11	13.1	0.08	11.0	3.68	0.03	0.06	6.0	3.86	0.01	38	0.01	27.7
3rd stems	8	0.11	30.5	0.26	27.0	9.21	0.26	0.01	19.5	7.24	0.0015	94	0.17	66.9
30/09/2008	17	0.09	31.3	0.18	28.2	8.69	0.10	0.06	17.7	7.38	0.0010	94	0.16	68.4
	31	0.17	32.9	0.18	27.1	9.92	0.21	0.12	19.7	7.56	0.0011	98	0.17	70.2
Average		0.12	31.5	0.20	27.4	9.27	0.19	0.06	19.0	7.39	0.0012	95	0.17	68.5
Std dev		0.04	1.2	0.05	0.7	0.62	0.08	0.06	1.1	0.16	0.00	2	0.01	1.6
4th stems	8	0.15	40.3	0.20	31.3	11.01	0.35	0.39	21.0	9.23	0.0000	114	0.19	83.2
08/12/2003	17	0.13	28.4	0.18	25.7	7.54	0.12	0.27	15.3	7.91	0.0014	86	0.18	62.1
	31	0.15	25.0	0.15	21.7	7.77	0.18	0.25	15.1	6.52	0.0012	77	0.18	54.9
Average		0.14	31.2	0.17	26.2	8.77	0.22	0.31	17.1	7.89	0.001	92	0.18	66.7
Std dev		0.01	10.8	0.04	6.8	2.29	0.12	0.10	4.2	1.92	0.00	26	0.01	20.0
5th stems	8	0.21	42.6	0.28	30.3	11.76	0.21	0.07	21.9	7.51	0.0000	115	0.15	85.0
12/10/2009	17	0.18	39.5	0.09	32.9	10.49	0.11	0.21	20.6	7.88	0.0013	112	0.17	83.2
	31	0.53	66.8	0.39	47.6	19.35	0.26	0.16	35.8	12.81	0.0010	184	0.14	134.2
Average		0.31	49.6	0.25	36.9	13.87	0.19	0.15	26.1	9.40	0.00	137	0.15	100.8
Std dev		0.22	17.1	0.08	12.2	5.37	0.03	0.07	9.8	3.75	0.00	49	0.00	34.8
6th stems	8	0.07	37.3	0.08	28.1	10.13	0.15	0.19	19.9	7.13	0.0000	103	0.16	75.8
18/01/2010	17	0.31	54.7	0.28	44.9	13.50	0.10	0.60	28.7	10.92	0.0048	154	0.19	114.0
	31	0.39	72.6	0.55	55.8	21.14	0.29	0.63	42.3	15.59	0.0014	209	0.16	150.8
Average		0.26	54.9	0.30	42.9	14.92	0.18	0.47	30.3	11.22	0.00	155	0.17	113.5
Std dev		0.23	25.0	0.33	19.6	7.78	0.10	0.31	15.9	5.99	0.00	75	0.00	53.0

APPENDIX E: SEM Images of different Genotypes of SRC Willow

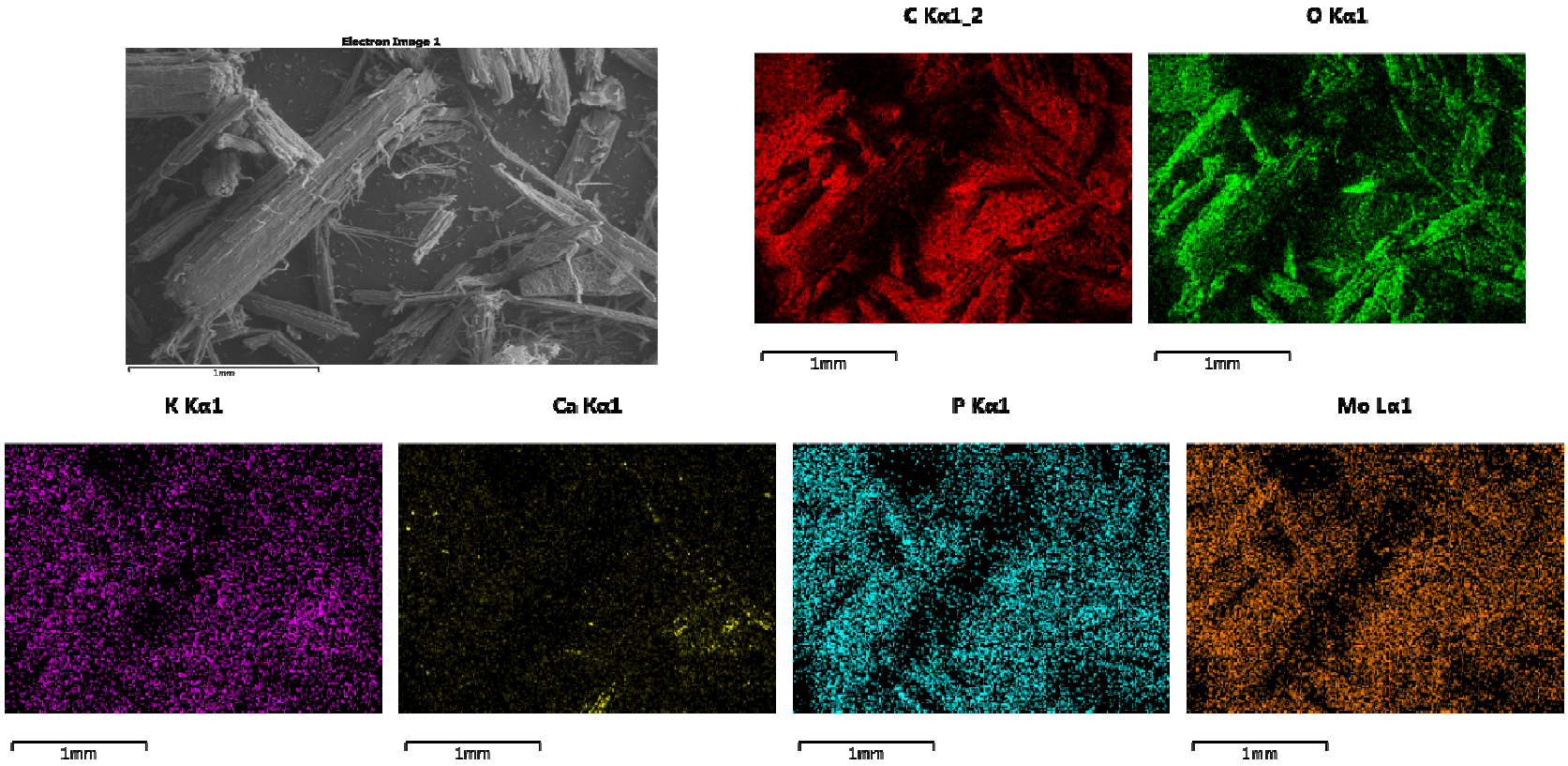


Figure E1 SEM images of raw material and dispersion of some metals in *S aurita L*

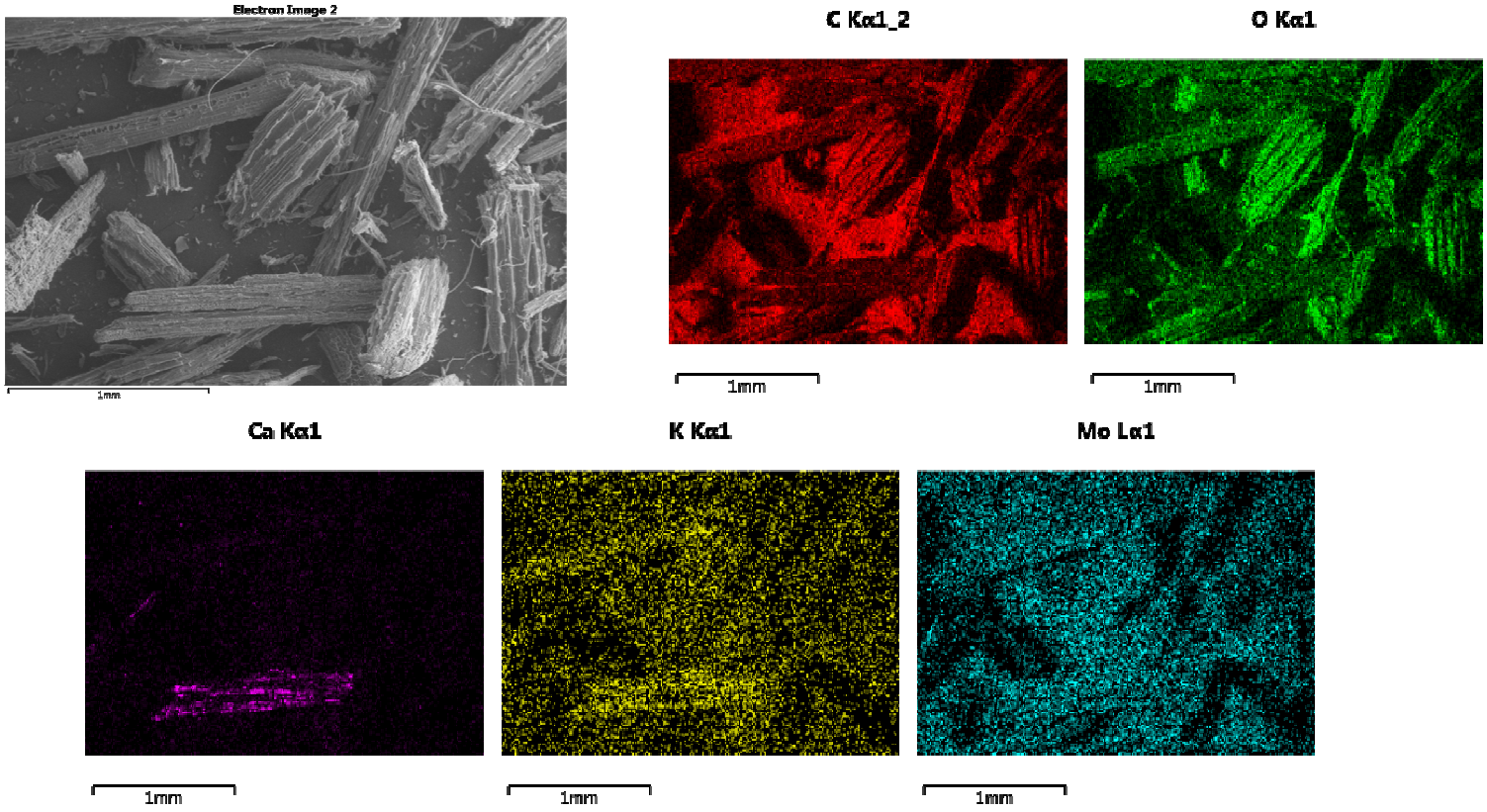


Figure E2 SEM images of raw material and dispersion of some metals in *S.viminalis x S.schwerinii*

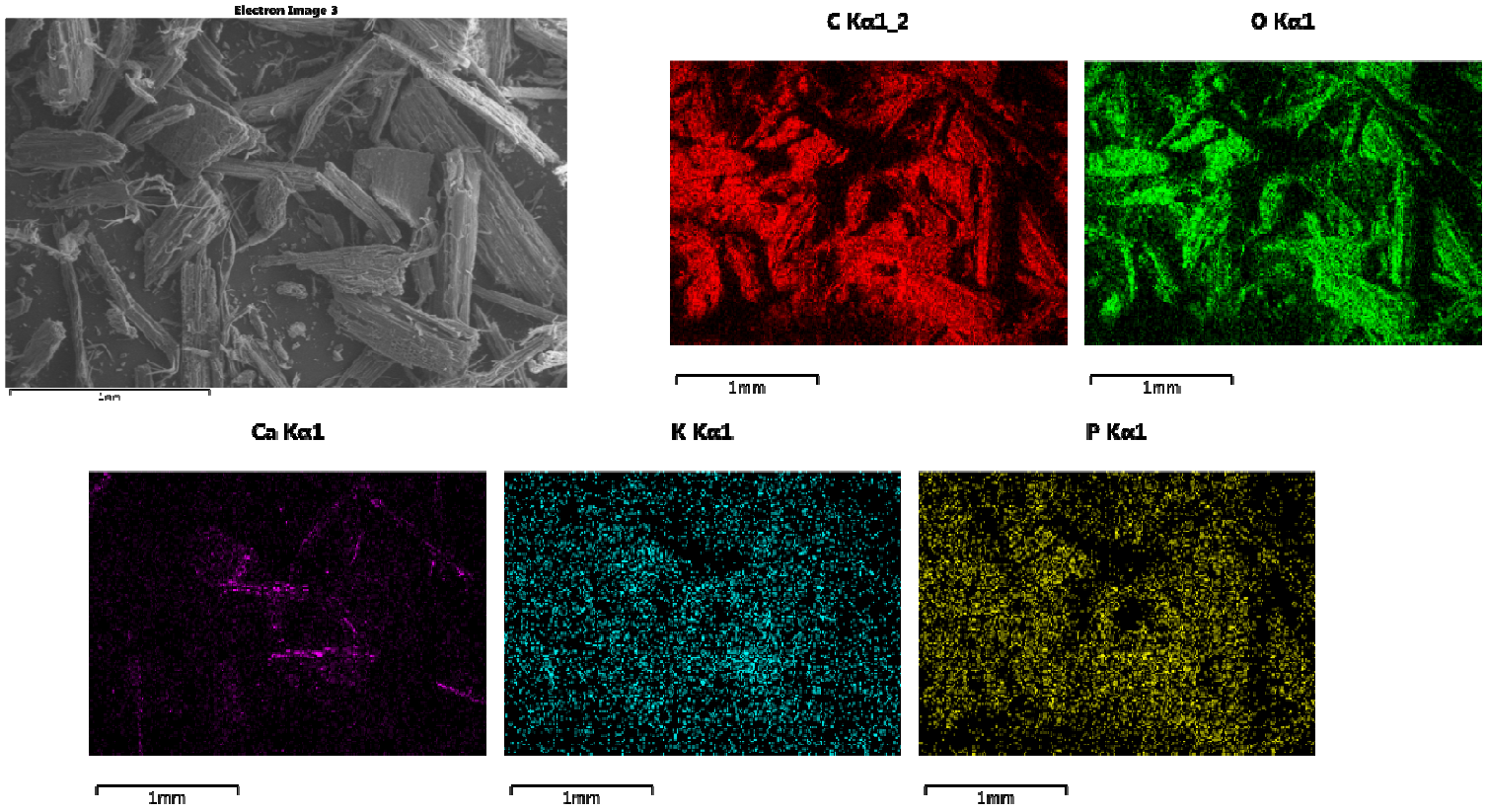
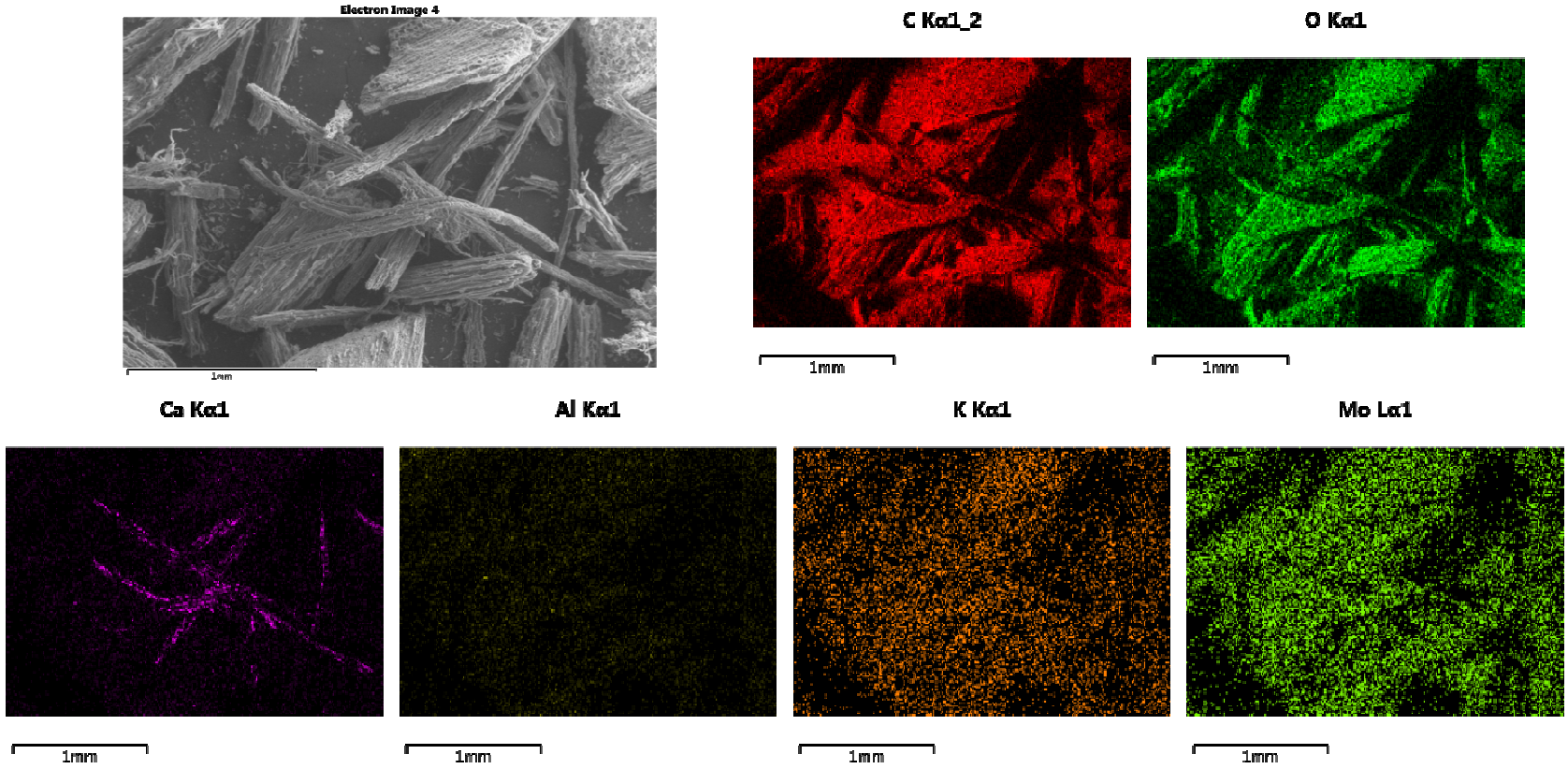


Figure E3 SEM images of raw material and dispersion of some metals in *S.eriocephala Michx*.


Electron Image 4
C Kα1_2
O Kα1
1mm
1mm
Ca Kα1
Al Kα1
K Kα1
Mo Lα1
1mm
1mm
1mm
1mm

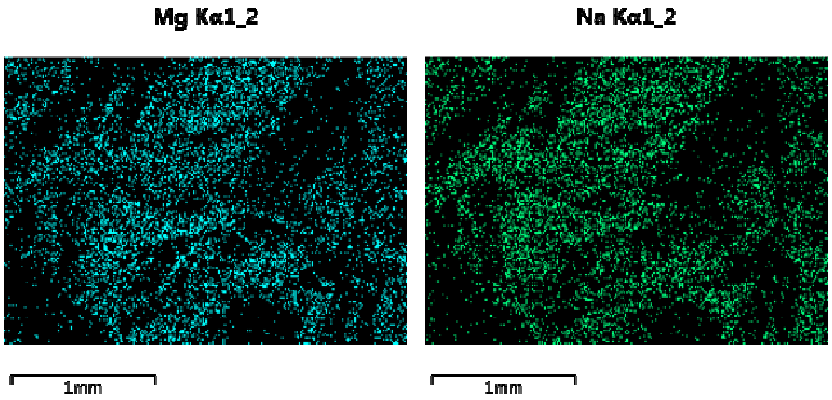
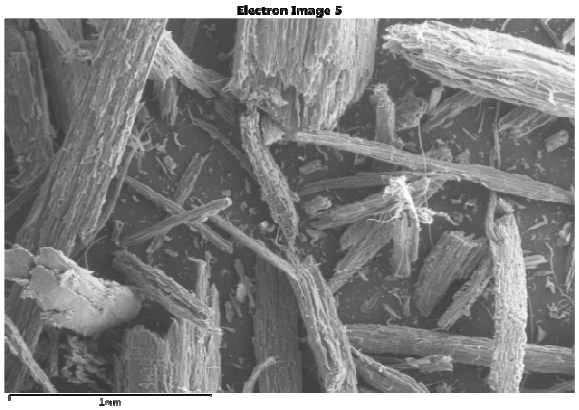
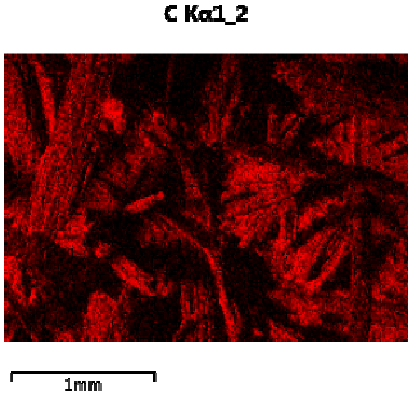
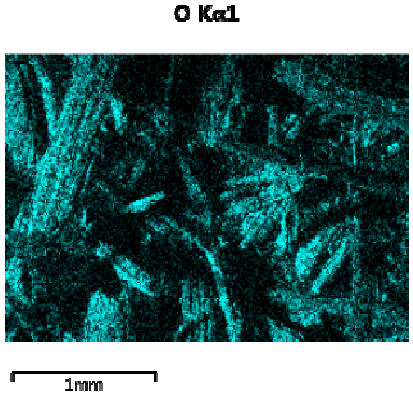
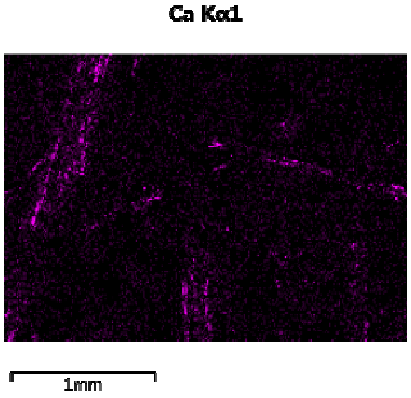


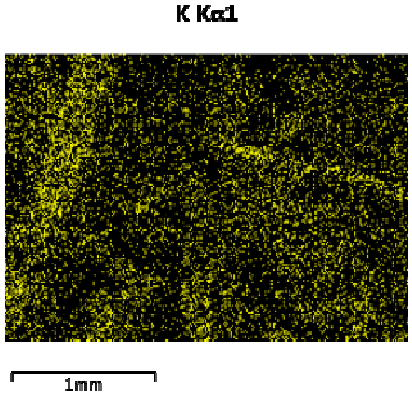
Figure E4 SEM images of raw material and dispersion of some metals in *S. Drummondiana Barratt ex Hook.*


Electron Image 5
1mm


C Kα1_2
1mm


O Kα1
1mm


Ca Kα1
1mm


K Kα1
1mm

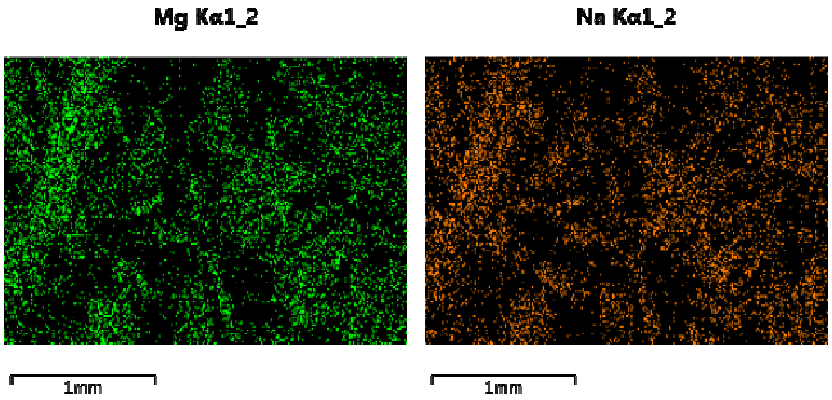


Figure E5 SEM images of raw material and dispersion of some metals in *S.mielichhoferii Saut.*